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EXPERIMENTAL DATA (FREQUENCY DOMAIN)

We have acquired sufficient theoretical foundation to understand and interpret the results of experimental measurements obtained in various materials. Both the dielectric constant and dielectric relaxation will be considered and results presented will follow, as far as possible, the sequence of treatment in the previous chapters. Anyone familiar with the enormous volume of data available will appreciate the fact that it is impossible to present all of the data due to limitations of space. Moreover, several alternative schemes are possible for the classification of materials for presentation of data. Phase classification as solids, liquids and gases is considered to be too broad to provide a meaningful insight into the complexities of dielectric behavior.

A possible classification is, to deal with polar and non-polar materials as two distinct groups, which is not preferred here because in such an approach we need to go back and forth in theoretical terms. However, considering the condensed phase only has the advantage that we can concentrate on theories of dielectric constant and dielectric loss factor with reference to polymers. In this sense this approach fits well into the scope of the book. So we adopt the scheme of choosing specific materials that permit discussion of dielectric properties in the same order that we have adopted for presenting dielectric relaxation theories. As background information a brief description of polymer materials and their morphology is provided because of the large number of polymer materials cited. We restrict ourselves to experimental data obtained mainly in the frequency domain with temperature as the parameter, though limited studies at various temperatures using constant frequency have been reported in the literature.

Measuring the real part of the dielectric constant centers around the idea that the theories can be verified using molecular properties, particularly the electronic polarizability, and the dipole moment in the case of polar molecules. A review of studies of dielectric loss is published by Jonscher¹ which has been referred to previously. The absorption

phenomena in gases and liquids in the microwave region has been treated by Illinger² and we restrict ourselves to the condensed phases.

The experimental techniques used to measure dispersion and relate it to the morphology, using electrical methods include some of the following:

1. Measurement of ϵ' and ϵ'' at various frequencies; each set of frequency measurement is carried out at a constant temperature and the procedure repeated isothermally at other selected temperatures (See fig 5.36 for an example). Plots of ϵ'' - $\log f$ exhibit a more or less sharp peak at the relaxation frequency. In addition the loss factor due to conductivity may exhibit a low frequency peak. The conductivity may be inherent to the polymer, or it may be due to absorbed moisture or deliberately increased in preparing the sample to study the variation of conductivity with temperature or frequency. Fig. 5.1 shows the loss factor in a thin film of amorphous polymer called polypyrrole³ in which the conductivity could be controlled by electrochemical techniques. The large conductivity contribution at low frequencies can be clearly distinguished. In this particular polymer the conductivity was found to vary according to $T^{-0.25}$. Care should be exercised, particularly in new materials, to distinguish the rise in ϵ'' due to a hidden relaxation.
2. Same as the above scheme except that the temperature is used as the variable in presenting the data and frequency as the parameter. Availability of computerized data acquisition equipment has made the effort less laborious. Fig. 5.2 shows this type of data for polyamide-4,6 which is a new material introduced under the trade name of Stanyl®⁴. Discussion of the data is given in section 5.4.11.
3. Three dimensional plots of the variation of ϵ' and ϵ'' with temperature and frequency as constant contours. This method of data presentation is compact and powerful for quickly evaluating the behavior of the material over the ranges of parameters used; however its usefulness for analysis of data is limited. Fig. 5.2 shows the contour plots of ϵ' and ϵ'' in Stanyl ® (Steeman and Maurer, 1992).
4. Measurement of polarization and depolarization currents as a function of time with temperature and the electric field as the parameters. Transformation techniques from time domain to the frequency domain result in data that is complimentary to the method in (1) above; the frequency domain data obtained this way falls in the low frequency region and is very useful in revealing phenomena that occur at low frequencies.

Examples of low frequency phenomena are α -relaxation and interfacial polarization, though care should be exercised to recognize ionic conductivity which is more pronounced at lower frequencies. For example the α -dispersion radian frequency in polystyrene is 3 s^{-1} at its glass transition temperature of 100°C . In this range of

frequency, time domain studies appear to be a more desirable choice. This aspect of dielectric study is treated in chapter 6.

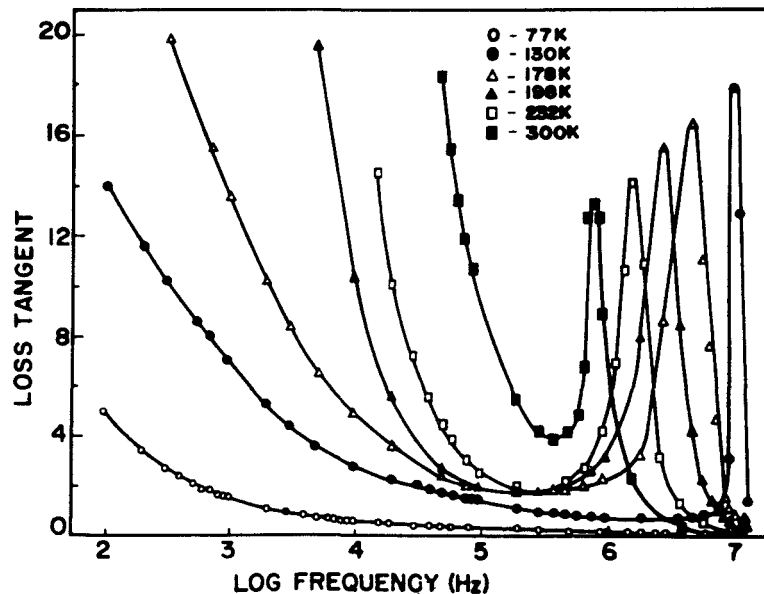


Fig. 5.1 Increase of low frequency loss factor in amorphous polypyrrole film (Singh et. al., 1991, with permission of J. Chem. Phys.)

5. Measurement of the ϵ'' - ω characteristic can be used to obtain the ϵ' - ω characteristics by evaluation of the dielectric decrement according to eq. (3.103) or Kramer-Kronig equations (equations 3.107 & 3.108). This method is particularly useful in relatively low loss materials in which the dielectric decrement is small and difficult to measure by direct methods. Two variations are available in this technique. In the first, $\epsilon(t)$ is measured, and by Fourier transformation $\epsilon^*(\omega)$ is evaluated. In the second method, $I(t)$ is measured and ϵ'' is then obtained by transformation. Integration according to eq. (3.107) then yields the dielectric decrement⁵.

6. Evaluation of the dielectric constant as a function of temperature by methods of (1) or (4) above and determining the slope $d\epsilon_s/dT$. A change of sign for the slope, from positive to negative as the temperature is increased, indicates a unique temperature, that of order-disorder transition.

7. The dielectric decrement at $\omega = 0$ is defined as $(\epsilon_s - \epsilon_\infty)$ and this may be evaluated by finding the area under ϵ'' - $\log\omega$ curve in accordance with eq. (3.103).

8. Presentation of dielectric data in a normalized method is frequently adopted to cover a wide range of parameters. For example the ϵ'' - $\log\omega$ curve is replotted with the x-axis showing values of $\omega/\omega_{\max}$ and y-axis showing $\epsilon''/\epsilon''_{\max}$. (see fig. 5.3⁶ for an example). If the points lie on the same curve, that is the shape of the curve is independent of

temperature, the symmetrical shape represents one of the Debye, Cole-Cole or Fuoss-Kirkwood relaxations.

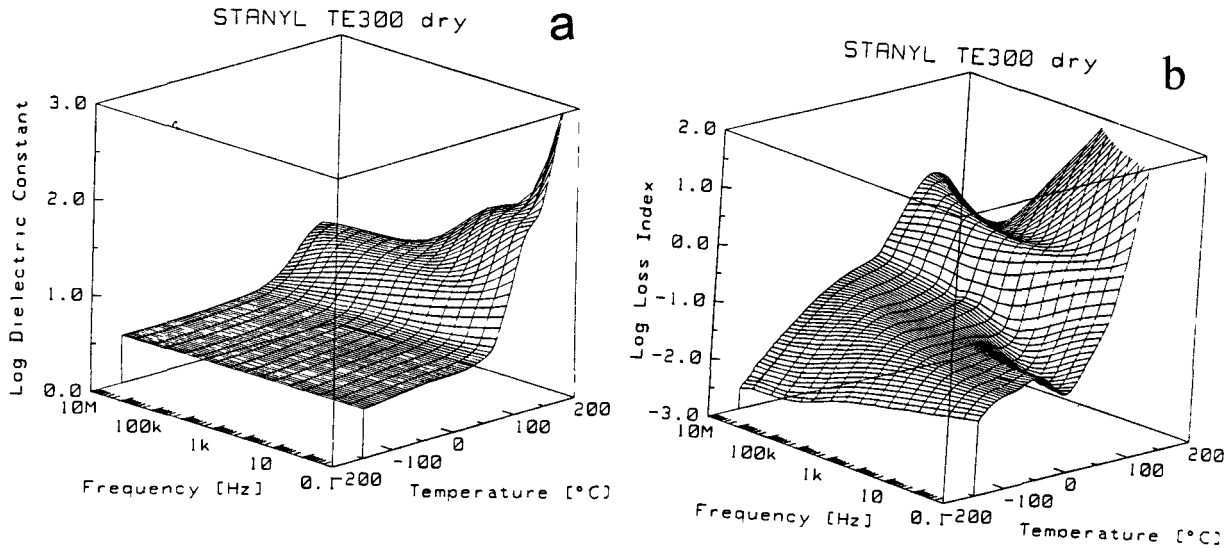


Fig. 5.2 (a) The dielectric constant of dry Stanyl® (aliphatic Polyamide) as a function of frequency and temperature. (b) The dielectric loss factor as a function of frequency and temperature (Steeman and Maurer, 1992, with permission of Polymer).

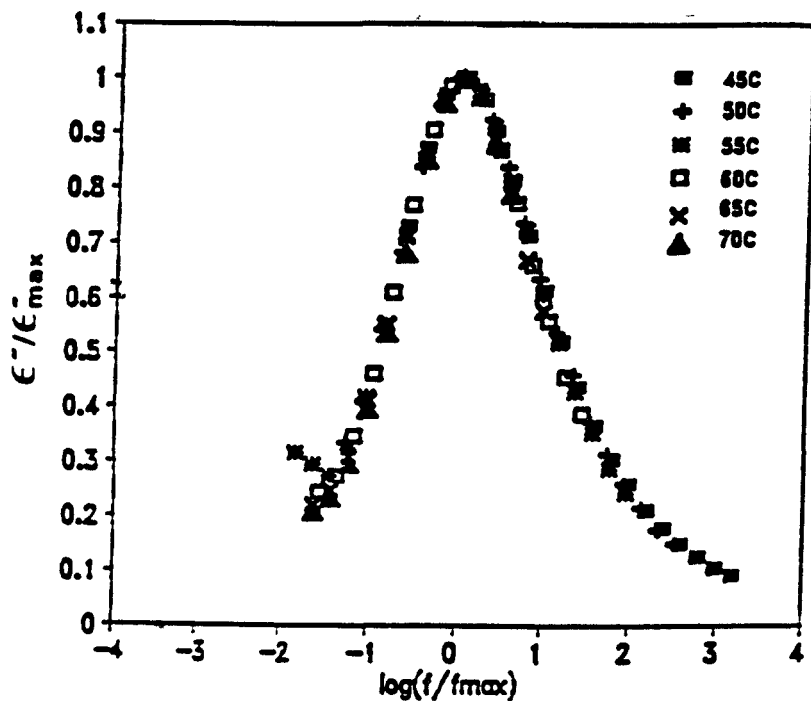


Fig. 5.3 Normalized loss factor in PVAc (Dionisio et. al. 1993, With permission of Polymer).

Another example is due to Jonscher's analysis of the data of Ishida and Yamafuji⁷ to discuss relaxation in PEMA as shown in Fig. 5.4. The normalized curves (b) show that the curve becomes broader as the temperature becomes smaller in the pre-peak region indicating strong evidence for overlap of another loss mechanism.

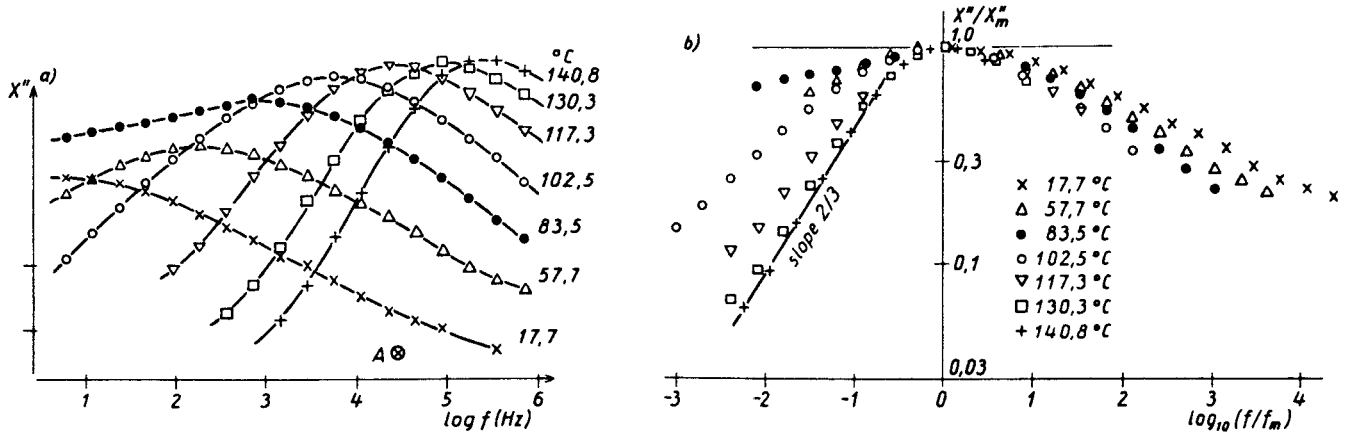


Fig. 5.4 (a) shows the dielectric loss data for poly(ethyl methacrylate) taken from Ishida and Yamafuji (1961). (b) shows the plots using normalized frequency and loss (Jonscher, 1983). (With permission of Chelsea Dielectric Press, London).

The normalization can be carried out using a different procedure on the basis of equations (3.86) as suggested by Havriliak and Negami⁸. In this procedure the co-ordinates are chosen as:

$$x = \frac{\epsilon' - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}}; \quad y = \frac{\epsilon''}{\epsilon_s - \epsilon_{\infty}}$$

If the data fall on a single locus then the distribution of relaxation times is independent of temperature.

Williams and Ferry et. al⁹ have demonstrated a relatively simple method of finding the most probable relaxation time. According to their suggestion the plots of the parameter $\epsilon''/(\epsilon_s - \epsilon_{\infty})$ versus T yields a straight line. The same dependence of reduced loss factor with temperature can exist only over a narrow range because at some low temperature the loss must become zero and it can not decrease further. At the other end the loss can reach a value of 0.5, or approach it, as dictated by Debye equation. A normalized loss factor greater than 0.5 is not observed because it would mean a relaxation narrower than the Debye relaxation.

With this overview we summarize the experimental data in some polymers of practical interest.

5.1 INTRODUCTION TO POLYMER SCIENCE

Polymers are found in nature and made in the laboratory. Rubber and cellulose are the most common example of natural polymers. One of the earliest polymers synthesized as a resin from common chemicals (phenol and formaldehyde) is called phenol formaldehyde (surprise!) commonly known as bakelite. Because of its tough characteristics bakelite found many applications from telephones to transformers. The vast number of polymers available today have a wide range of mechanical, thermal and electrical characteristics; from soft and foamy materials to those that are as strong as steel, from transparent to completely opaque, from highly insulating to conducting. The list is long and the end is not in sight.

5.1.1 CLASSIFICATION OF POLYMERS

Polymers may be classified according to different schemes; natural or synthetic, organic or inorganic, thermoplastic or thermosetting, etc. Organic molecules that make fats (**aliphatic** in Greek) like waxes, soaps, lubricants, detergents, glycerine, etc. have relatively straight chains of carbon atoms. In contrast **aromatic** compounds are those that were originally synthesized by fragrances, spices and herbs. They are volatile and highly reactive. Because they are ready to combine, aromatics outnumber aliphatics. Molecules that have more than six carbon atoms or benzene ring are mostly aromatic. The presence of benzene in the backbone chain makes a polymer more rigid.

Hydrocarbons whose molecules contain a pair of carbon atoms linked together by a double bond are called **olefins** and their polymers are correspondingly called **polyolefins**. Polymers that are flexible at room temperature are called **elastomers**. Natural rubber and synthetic polymers such as polychloroprene and butadiene are examples of **elastomers**. The molecular chains in elastomers are coiled in the absence of external force and the chains are uncoiled when stretched. Removal of the force restores the original positions. If the backbone of the polymer is made of the same atom then the polymer is called a **homochain** polymer, as in polyethylene. In contrast a polymer in which the backbone has different atoms is known as a **heterochain** polymer.

Polymers made out of a single monomer have the same repeating unit throughout the chain while polymers made out of two or more monomers have different molecules along the chain. These are called **homopolymers** and **copolymers** respectively. Polyethylene, polyvinyl chloride (PVC) and polyvinyl acetate (PVAc) are homopolymers. Poly (vinyl chloride-vinyl acetate) is made out of vinyl acetate and vinyl chloride and it is a copolymer.

Copolymers are classified into four categories as follows:

1. **Random copolymer:** In this configuration the molecules of the two comonomers are distributed randomly.
2. **Alternating copolymer:** In this structure the molecules of the comonomers alternate throughout the chain.
3. **Block copolymer:** The molecules of comonomers combine in blocks, the number of molecules in each block generally will not be the same.
4. **Graft copolymer:** The main chain consists of the same monomer while the units of the second monomer are added as branches.

For the ability of a monomer to turn into polymer, that is for polymerization to occur, the monomer should have at least two **reactive sites**. Another molecule attaches to each of the reactive sites and if the molecule has two reactive sites it is said to have **bifunctionality**. A compound becomes reactive because of the presence of reactive functional groups, such as --OH , --COOH , --NH_2 , --NCO etc. Some molecules do not contain any reactive functional groups—but the presence of double or triple bonds renders the molecule reactive. Ethylene (C_2H_6) has a double bond and a functionality of two. Depending on the functionality of the monomer the polymer will be linear if bifunctional, branched or cross linked in three dimensions if tri-functional. If we use a mixture of bi-functional and tri-functional monomers the resulting polymer will be branched or cross linked depending on their ratio.

When monomers just add to each other during polymerization the process is called **addition** polymerization. Polyethylene is an example. If the molecules react during the polymerization the process is known as **condensation** polymerization. The reacting molecules may chemically be identical or different. Removal of moisture during polymerization of **hydroxy** acid monomers into polyester is an example. Polymerization of nylon from adipic acid ($\text{C}_6\text{H}_{10}\text{O}_4$) and hexamethylenediamine ($\text{C}_6\text{H}_{16}\text{N}_2$) is a second example. In addition polymerization, the molecular mass of the polymer is the mass of the monomer multiplied by the number of repeating units. In the case of condensation polymerization, this is not true because condensation or removal of some reaction products reduces the molecular mass of the polymer.

The chemical structure of a polymer depends on the elements in the monomer unit. In polymers we have to distinguish between the chemical structure and the geometrical structure because of the fact that monomers combine in a particular way to yield the polymer. Two polymers having the same chemical formula can have different geometrical arrangement of their molecules. Two terminologies are commonly used; **configuration** and **conformation**. Configuration is the arrangement of atoms in the adjacent monomer units and it is determined by the nature of the chemical bond between adjacent monomer units and between adjacent atoms in the monomer. The configuration

of a polymer cannot be changed without breaking the chemical bonds; it is equivalent to changing its finger print, its identity, so to speak.

A conformation is one of several possible arrangements of a chain segment resulting from rotation around a single bond. A change in conformation does not involve breaking or reforming any bond and the rotation of the segment occurs only in space. A polymer of given conformation can assume several different configurations over a period of time depending upon external factors such as thermal energy, mechanical stress, etc.

The conformation assumed by a polymer depends upon whether the polymer is a **flexible chain** type or **rigid chain** type. In a flexible chain type the chain segments have sufficient freedom to rotate about each other. Polymers that have non-polar segments or segments with low dipole moments are flexible chain type. Polyethylene, polystyrene and rubber belong to this class. On the other hand, rigid chain polymers have chain segments in which rotation relative to each other is hindered due to a number of reasons. The presence of bulky side groups or aromatic rings in the back bone acts as hindrance to rotation. Strong forces such as dipole attraction or hydrogen bonding also prevent rotation. Polyimides, aromatic polyesters and cellulose esters belong to this category.

Conformations of polymers in the condensed phase vary from a rigid, linear, rod like structure to random coils that are flexible. In amorphous solids the coils are interpenetrating whereas in crystalline polymers they are neatly folded chains. In dilute solutions molecules of flexible chain, polymers exist as isolated random coils like curly fish in a huge water tank. Molecules of rigid chain polymers in solution exist as isolated stiff rods or helixes.

Stereo-regular polymers, or stereo polymers for short, have the monomers aligned in a regular configuration giving a structural regularity as a whole. The structure resembles cars of the same model, and same color parked one behind the other on a level and straight road. In a non-stereo polymer the molecules are in a random pattern as though identical beads are randomly attached to a piece of flexible material that could be twisted in several different directions.

Chemical compounds that have the same formula but different arrangement of atoms are called **isomers**. The different arrangement may be with respect to space, that is geometry; this property is known as **stereo-isomerism**, sometimes known as geometric isomerism. Stereo-isomerism has a relation to the behavior of light while passing through the material or solution containing the material. It is known in optics that certain crystals, liquids or solutions rotate the plane of plane-polarized light as the light passes through the material. The origin of this behavior is attributed to the fact that the molecule is asymmetric, so that they can exist in two different forms, each being a

mirror of the other. The two forms are known as **optical isomers**. If one form rotates the plane of plane-polarized light clockwise, the form is known as **dextro-rotatory (prefix-*d*)**. The other form will then rotate the plane in the anti-clockwise direction by exactly the same amount; This form is known as **laevo-rotatory (prefix-*l*)**. A mixture of equal molar volume of **D** and **L** forms of the same substance will be optically neutral. If the position of the functional group is different or the functional group is different then the property is called **structural isomerism**. There are a number of naturally occurring isomers but they occur only in *d* or *l* forms, not both.

To describe **isomerism** in polymers we choose polyethylene because of its simple structure. The carbon atoms lie in the plane of the paper, though making an angle with each other, which we shall ignore for the present. The hydrogen atoms attached to carbon, then, lie above or below the plane of the paper. It does not matter which hydrogen atom is above the plane and which below the plane of the paper because, in polyethylene the individual hydrogen atoms attached to each carbon atom are indistinguishable from each other.

Let us suppose that one of the hydrogen atoms in ethylene is replaced by a substituent R (R may be Cl, CN or CH₃). Because of the substitution, the structure of the polymer changes depending upon the location of R with regard to the carbon atoms in the plane of the paper. Three different structures have been identified as below (Fig. 5.5¹⁰).

1. R lies on one side of the plane and this structure is known as **isotactic configuration**. This is shown in Fig. (5.5 a).
2. R lies alternately at the top and bottom of the plane and this structure is known as **syndiotactic configuration** (Fig. 5.5 b).
3. R lies randomly on either side of the plane and this structure is known as the **atactic** or **heterotactic** configuration (Fig. 5.5 c).

Though the chemical formula of the three structures shown are the same, the geometric structures are different, changing some of its physical characteristics. Atactic polymers have generally low melting points and are easily soluble while isotactic and syndiotactic polymers have high melting points and are less soluble.

5.1.2 MOLECULAR WEIGHT AND SIZE

The number of repeating units of a molecule of polymer is not constant due to the fact that the termination of polymerization of each unit is a random process. The molecular mass is therefore expressed as an average based on the number of molecules or the mass of the molecules. The **number average** molecular mass is given by

$$M_{av\ n} = \sum \frac{n_i m_i}{n_i} \quad (5.1)$$

Where n_i and m_i are the number and mass of the i^{th} repeating unit respectively. The mass average molecular mass is given by

$$M_{av,m} = \frac{\sum n_i m_i^2}{\sum n_i m_i} \quad (5.2)$$

For synthetic polymers $M_{av,m}$ is always greater than $M_{av\ n}$. For these two quantities to be equal requires that the polymer should be homogenous, which does not happen. The mechanical strength of a polymer is dependent upon the number of repeating units or the degree of polymerization.

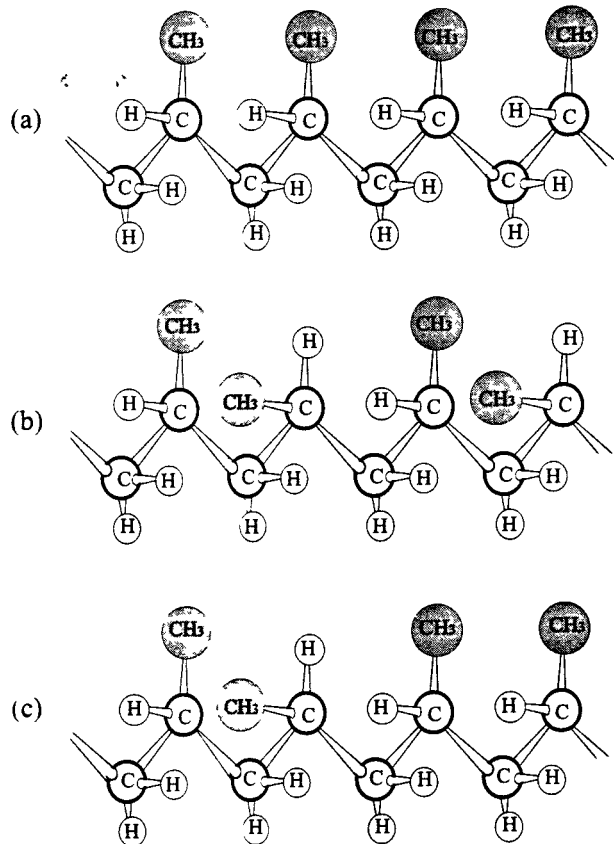


Fig. 5.5 Three different stereoregular structures of polypropylene: (a) isotactic, CH₃ groups are on the same side of the plane C=C bond (b) Syndiotactic, CH₃ groups alternate on the opposite of the plane (c) atactic, CH₃ groups are randomly distributed (Kim and Yoshino, 2000) (with permission of J. Phys. D: Appl. Phys.)

A substance that has the same mass for each molecule is called a **mono-dispersed** system. Water is a simple example. In contrast, polymers have molecules each with a different mass. Such substances are called poly-dispersed systems. However, certain polymers can be polymerized in such a way that they are mono-dispersed. Polystyrene is an example of this kind of polymer.

A polymer chain can assume different shapes. At one end of the spectrum the molecule may be fully extended while at the other end it may be tightly coiled. Random walk theory shows that these extreme shapes occur with very low probability while a randomly coiled shape is more common.

5.1.3 GLASS TRANSITION TEMPERATURE

Solids and liquids are phase separated at the melting point. Polymers have an intermediate boundary called the **glass transition temperature** at which there are remarkable changes in the properties of the polymers. In a simplistic view this is the temperature at which a needle can be inserted into the otherwise hard polymer, such as polystyrene. Of course this method of determining the glass transition temperature is not scientifically accurate and other methods must be employed. The transition does not have latent heat and does not show change in thermodynamic parameters or x-ray diffraction pattern. However the **specific volume**, defined as the inverse of specific density, shows an abrupt increase with increasing temperature. This method of determining the transition temperature by various experimenters gives results within a degree.

In a crystalline solid, at low temperatures, the molecules occupy well defined positions within the crystal lattice in three dimensions, though they vibrate about a mean position. Long range order is said to exist within the crystal and there is no **Brownian motion**. In view of the rigidity of the solid any applied external force, below yield stress, will be transferred without disruption of the lattice structure.

As the temperature is increased kinetic energy is added to the system and the molecules vibrate more energetically. A point is reached eventually when the vibrational motion of the molecule can exceed the energy holding the molecule in its position within the lattice. The molecule is now free to float about and this is the onset of Brownian motion. At a higher temperature still, the motion of molecules spreads in the lattice and the long range order is lost. At this temperature, called the **melting point**, the system will yield to any external force and flow.

In a polymer with large molecules, such as polyethylene, an intermediate state between solid and liquid phases exists, with segments of a chain moving. The large molecule is still immobile with motion of chain segments confined to local regions. This state is referred to as the **rubbery state**. Though the long range order of the solid is lost there is still some order. Some segments of a long chain molecule may have freedom of movement while the molecule itself is not free to move. Only when the temperature is increased still higher does the polymer melt into a highly viscous fluid with the entire chain moving. From the point of view of dielectric studies, our interest lies in the temperature range below and just above the glass transition temperature, unless of course the polymer is a liquid at operating temperature.

5.1.4 CRYSTALLINITY OF POLYMERS

As explained above crystalline solids possess long range order. At low temperatures the molecules are immobile due to intermolecular forces. At high temperatures the energy required to impart mobility is almost equal to the melting point and therefore the rubbery state exists over a very narrow temperature range. In polymers the situation is quite different due to the fact that most polymers are not usually entirely crystalline or amorphous. They are partially crystalline and contain regions that are both crystalline and amorphous. For example in polyethylene prepared by the high pressure method crystallinity is about 50% with both crystalline and amorphous material present in equal amounts. The region of crystallinity is about 10-20 nm¹¹.

In high polymers measurement of conductivity on seemingly identically prepared specimens show considerable scatter in the activation energy and conductivity. It has been realized that the morphology of the polymer is the influencing factor even though all the experimental conditions are kept identical. While the chemical structure can be maintained the same, the crystallinity of a sample is not easy to reproduce except for single crystals. Fig. 5.6¹² shows the dependence of crystallinity on the rate of cooling of polyethylene produced from melt. The width of each square is the maximum uncertainty. Both crystallinity and density increases with decreasing cooling rate.

Partially crystalline polymers possess both a glass transition temperature and a melting point. If the temperature of the polymer $T < T_g$, the amorphous regions exist in the glassy state and the crystalline regions remain crystalline. Molecular motion in this temperature region is limited to rotation of side groups or parts of side group. Another kind of motion called 'crankshaft' motion of the main chain is also possible below the glass transition temperature; 'crankshaft' motion is the rotation of the four inner carbon atoms even though the outer atoms remain stationary [Bueche, 1962]. At $T \sim T_g$ the amorphous regions become rubbery with no appreciable change in the crystalline regions. The space between molecules or free volume must increase to allow for motion

of molecular chain. At $T > T_m$ the distinction between the amorphous and crystalline regions disappears because the polymer melts.

Crystalline polymers obtained from melts do not show anything extraordinary when viewed in a microscope with unpolarized light. However when a polarizing microscope is used complex polycrystalline regions are observed. The regions have high geometrical symmetry, roughly 1 mm in diameter, circular in shape. They are regions of birefringence. The regions resemble a four sector ceiling fan and are called **spherulites** (fig. 5.7). They are believed to be made of several inter-connected lamellae which are stacked one upon the other like the pages of a book. Their presence is an evidence of crystallinity of the polymer. The spherulites keep growing spherically till they collide with another spherulite and the growth stops. It is generally believed that spherical spherulites are formed as the polymer crystallizes in the bulk [Bueche, 1962].

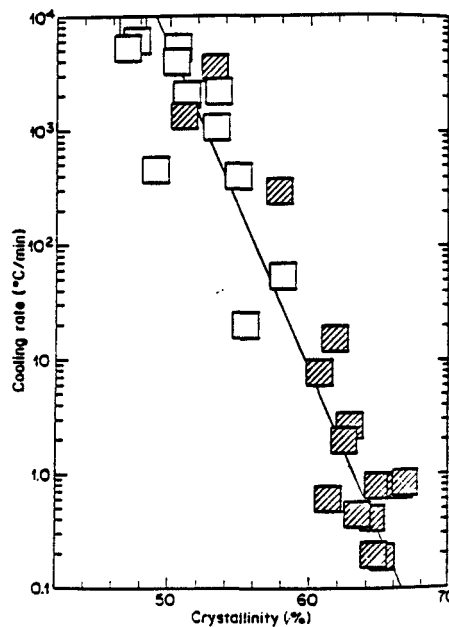


Fig. 5.6 Rate of cooling from the melt versus percent crystallinity in 3% carbon filled polyethylene (H. St. Onge, 1980, with permission of IEEE ©).

Single crystals of some polymers can be obtained from very dilute solutions by crystallization. When examined under electron microscope the minute crystals revealed thin slabs or lamellae. X-ray studies of the **lamellae** revealed, quite unexpectedly that the molecular chain was perpendicular to the plane of the slab. Since the length of a chain (100-1000 nm) was several times the transverse thickness of the slab (10 nm), the molecular chain must fold making a round about turn at the edges. The spacing between folds and therefore the thickness of the lamellae is extremely regular. At the fold surface the long molecule does not fold neatly but makes distorted 'U' type loops or leave loose ends. This is a region of disorder even in a single crystal.

The configuration of the chain of the polymer determines whether the polymer is crystalline. Table 5.1 lists the glass transition temperature of some crystalline and amorphous polymers.

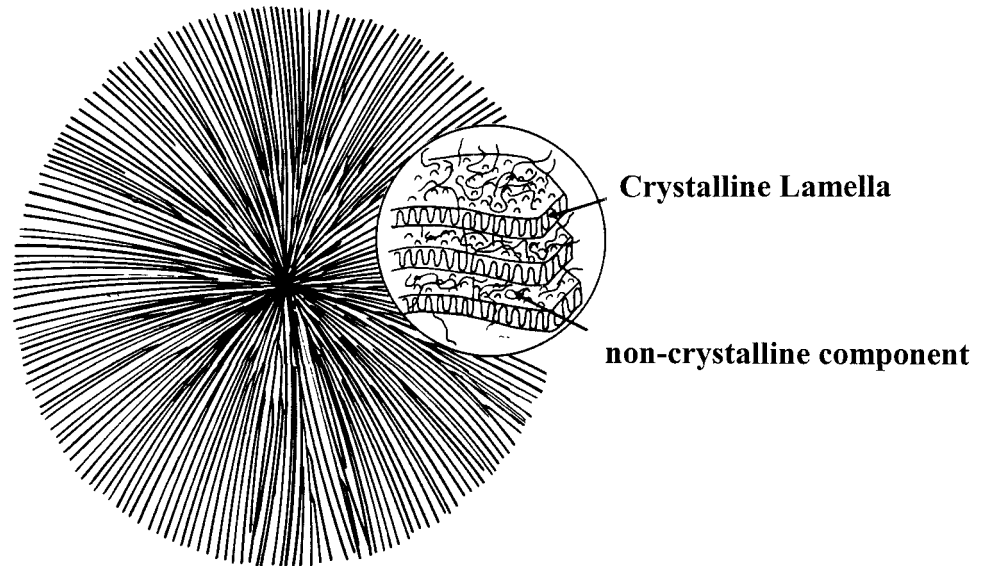


Fig. 5.7. Schematic Spherulite structure in semi crystalline polymers. Molecular chain axes are approximately normal to the surfaces of the Lamellar platelets which grow radially from the center of the structure. (Broadhurst and Davis, 1980, with permission of Springer Verlag, Berlin).

Accepting the view that crystallization in the bulk occurs via spherulites and single crystallization occurs via lamallae, the relation between spherulites and lamallae needs to be clarified. We recall that bulk crystallization is obtained from melts and single crystallization from very dilute solutions. It is reasonably certain that the growth begins at a single nucleus and ribbon like units propagate developing twists and branches. A spherical pattern is quickly established and folded chains grow at right angles to the direction of growth. Spherulites are complicated assemblies of lamallae and amorphous materials exist between fibrous crystals. The region between spherulites themselves is also filled with amorphous materials. Growth of a Spherulite ceases when its boundy overlaps that of the next [Bueche, 1962].

Table 5.1 leads to the question: What is the relationship of T_g to T_m ? From a number of experimental results the relation

$$\frac{1}{2} < \frac{T_g}{T_m} < \frac{2}{3} \quad (5.3)$$

has been found useful to estimate the glass transition temperature.

Table 5.1
Glass Transition Temperature of Polymers

Polymer	T _g (°C)	T _m (°C)
polyisoprene (Natural Rubber)	-73	36
Nylon 6 (Polyamide 6)	50	250
Nylon (6,6)	50	270
Polyvinyl chloride	81	310
Polytetrafluoroethylene		
Polybutadiene (trans-)	-58	100
Polybutyl acrylate	-54	47
Polycarbonate (bisphenol-A)	145	265
Polychlorotrifluoroethylene (PCTFE)	40-59	185-218
Polyethylene (high density)	-125	146
Polyethylene terephthalate	69-75	264
polyamide	90	295
Polyimide	260-320	
Polymethyl methacrylate		
atactic	105	-
isotactic	38	160
syndiotactic	105	>200
Polypropylene (PP)		
atactic	105	-
isotactic	-8	208
Polystyrene	100	250
Polyvinyl acetate	32	-
Polyvinyl alcohol		
Atactic	85	-
Isotactic		212
syndiotactic		267

Amorphous polymers generally exhibit three different relaxations, called α -, β - and γ -relaxation in order of decreasing temperature or increasing frequency. At the glass transition temperature there is a rapid increase in viscosity if the polymer is being cooled and the main relaxation, α -relaxation, slows down. The faster relaxation, β -relaxation, also occurs below T_g and has a much weaker temperature dependence. The splitting of the two relaxations has been observed to occur in three different ways, as shown in fig. 5.8¹³.

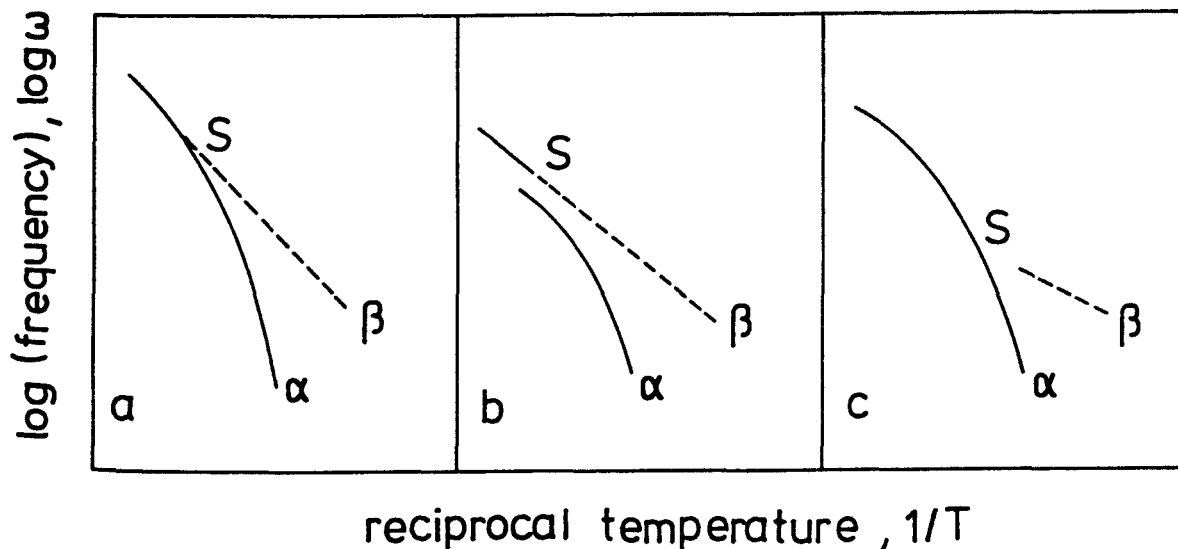


Fig. 5.8 Splitting of the α -, and β -relaxation in amorphous polymers, from high to low temperature (a) true merging of the two relaxations leading to a single high temperature process, (b) Separate onset of the α - transition, (c) Classical β -relaxation stimulated by the development of the α -process. S is the splitting region (Garwe et. al. 1994, with permission of Inst. of Phys., England).

The β -relaxation follows Arrhenius law ($\log \tau \propto 1/T$) and the ϵ'' - $\log(\omega)$ curve is symmetrical on either side at the maximum. On the other hand, the ϵ'' - $\log(\omega)$ curve is asymmetric with a high frequency broadening. The α -relaxation time follows a non-Arrhenius behavior that is normally described by the Vogel-Fulcher (VF) equation (5.18) or the WLF equation (5.19), presented in sections (5.4.5) and (5.4.7) respectively. A detailed discussion of the relaxation laws is deferred to maintain continuity.

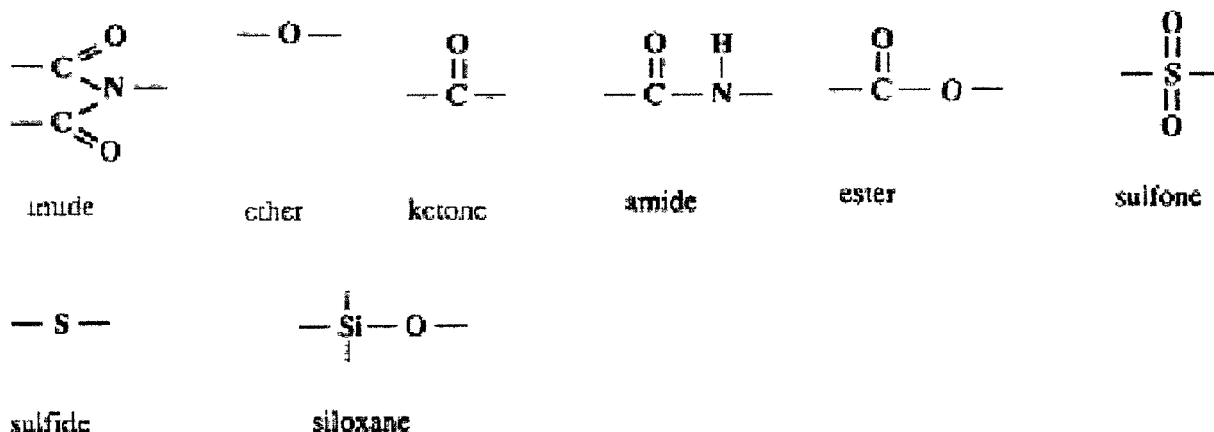
5.1.5 THERMALLY STABLE GROUPS

Certain chemical groups are known to increase thermal resistance, and by increasing these groups, polymers with high thermal stability have been synthesized. Some of these groups are shown below.

5.1.6 POLYMER DEGRADATION AND DEFECTS

Degradation and defects are topics of vital interest in engineering applications. A Polymer degrades basically by two methods: (1) **Chain end degradation** (2) **Random degradation**. Chain degradation consists of the last monomer in the chain dropping out and progressively the chain gets shorter. This is the inverse process of polymerization. This mode of degradation is often termed as **depolymerization** or **unzipping**, the latter term having the connotation that polymerization is a zipping process. Often the degradation is accelerated by higher temperature, presence of moisture, oxygen and carbon dioxide. For example poly(methyl methacrylate) degrades at 300°C releasing an

almost equal amount of monomer. Recycling polymers involves recovering the monomer and polymerizing again.



Thermally stable groups (R. Wicks, "High Temperature Electrical Insulation", (unpublished) Electrical Insulation Conference/ International Coil Winders Association, 1991, with permission of IEEE ©).

Random degradation is initiated at any point along the chain and is the reverse process of polymerization by poly-condensation process. This kind of degradation can occur in almost all polymers. In random degradation of polyethylene a hydrogen atom may migrate from one carbon atom to another elsewhere along the chain and cause chain scission yielding two fragments. Polyesters absorb moisture and chain scission occurs. The causes for degradation may be classified as follows:

1. Thermal degradation
2. Mechanical degradation
3. Photodegradation
4. Degradation due to radiation
5. Degradation due to oxidation and water absorption.

The stability of bonds in the chain is a vital parameter in determining the degree of thermal degradation. For C-C bonds a simple rule is enough for our purpose: more bonds give less stability. A single bond is stronger than a double bond or a triple bond. Increasing the number of constituents in the backbone also decreases stability. Polyethylene is thermally more stable than polypropylene; in turn polypropylene is more stable than polyisobutylene (see the Table of formulas 5.3). Bond dissociation energies for C—C are shown in Table 5.2 and the simple ideas stated above are found to be generally true for molecules containing a H atom. If the molecule does not contain H at all (Teflon is an example) then other considerations such as electronegativity enter the picture. The last entry in Table 5.2 is included to illustrate this point.

Polymers with aromatic groups in the backbone are generally more stable thermally. Poly(phenylene) which has only aromatic rings in the backbone also has high thermal stability. Poly(tetrafluorophenylene) which combines the characteristics of PTFE and poly(phenylene) is even more stable, up to 500°C. Fig. 5.9¹⁴ (Sessler 1980) shows the types of defects that occur in polymers.

5.1.7 DIPOLE MOMENT OF POLYMERS

We are now ready to consider the dipole moment of polymer molecules. We have already shown (Ch. 2) that the dielectric constant of a polar liquid is higher than a non-polar liquid because the dipoles align themselves in an electric field. The same concept can be extended to polymers with polar molecules, in the molten state. In the condensed phase the molecules arrange themselves in a given configuration and eq. (2.54) shows that the polarization due to dipoles is proportional to $N\mu^2$ where N is the number of molecules per unit volume and μ the dipole moment.

For the purpose of continuity it is convenient to repeat the Clausius-Mosotti ratio

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{N\alpha_e}{3\epsilon_0} + \frac{N\mu^2}{9\epsilon_0 kT} \quad (2.54)$$

Table 5.2
Dissociation Energies of C—C, C-F Bonds

Molecule	Energy (eV)
CH ₃ —CH ₃	3.82
CH ₃ CH ₂ —CH ₃	3.68
(CH ₃) ₃ C—CH ₃	3.47
C ₆ H ₅ CH ₂ —CH ₃	3.04
CF ₄	4.68

Let us consider the variation of the term in brackets on the right side in the case of a polymer that has been polymerized by Z monomer units, each having a dipole moment of μ . We assume that μ is unaffected by the process of polymerization. Before polymerization the aggregate of Z monomers make a contribution of $Z\mu^2$ to the second term in equation (5.1).

After polymerization the contribution of this term depends upon one of the three possibilities:

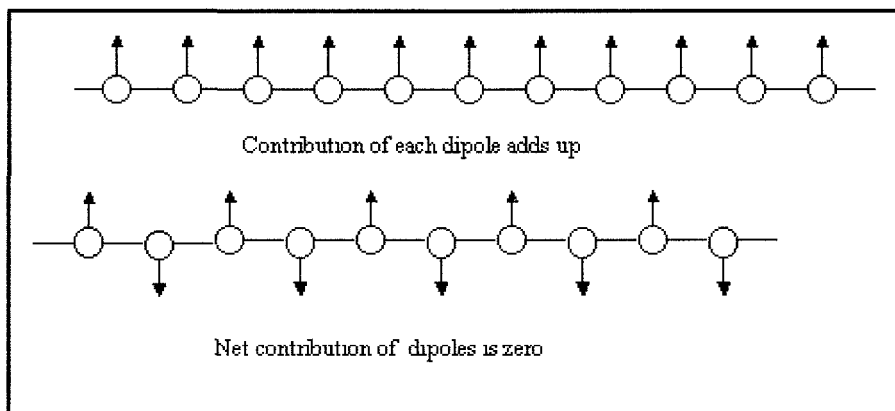
- (1) The dipoles are rigidly fixed aligned in the same direction. The contribution of Z units is $Z^2\mu^2$.
- (2) The dipoles are aligned in such a way that their dipole moments cancel; the contribution is zero.
- (3) The dipoles are completely free to rotate, each dipole making a contribution of μ^2 ; the contribution of Z units is $Z\mu^2$, (see box below).

Thus the dipole moment contribution can vary from zero to $Z^2\mu^2$. An infinitely large variation is possible depending upon the configuration of the polymer. To put it another way the dipole moment of a polymer provides information as to the structure of the chain. The average dipole moment of a polymer containing Z number of units, each possessing a dipole moment μ , is given by [Bueche, 1962] as

$$\mu_{av}^2 = \left\langle \sum_{n=1}^Z \sum_{m=1}^Z \mu_n \cdot \mu_m \right\rangle_{av} \quad (5.4)$$

where the symbolism $\langle \mu_n \cdot \mu_m \rangle_{av}$ is the average value of the product $\mu_n \mu_m \cos \theta$ over all chain configurations, where θ is the angle between dipoles with index n and m .

For a freely jointed molecule it is easy to see that $\mu_{av}^2 = Z\mu^2$, that is the contribution of the monomer unit in the polymer, is equal to the dipole moment of the monomer unit in the un-polymerized state. For other configurations the average dipole moment contribution is found to be $\mu_{av}^2 = k Z\mu^2$ where k is a constant. Actual measurements show that $k = 0.75$ for poly (vinyl chloride).



A few general comments with regard to the dielectric loss factor of polymers is appropriate here. We have already explained that the glass transition temperature induces segmental motion in the chain and a jump frequency ϕ may be defined as the number of jumps per second a segment translates from one equilibrium position to the

other. ϕ depends on the molecular mass, in the range of 10^{-3} - 10 /s. The jump distance δ is the average distance of the jump. δ will not vary much from material to material, 10-100 nm.

As an approximation we can assume that the dipoles are rigidly attached to the chain segment, as in poly(vinyl chloride) for example. The implication of this assumption is that the dipoles move with essentially the same rate as the segment. Further, in accordance with Frohlich's theory (fig. 3-5) it is assumed that the dipoles are oriented parallel or anti-parallel to the applied field. The dielectric loss is a maximum at the radian frequency

$$\omega_{\max} = 2\phi \quad (5.5)$$

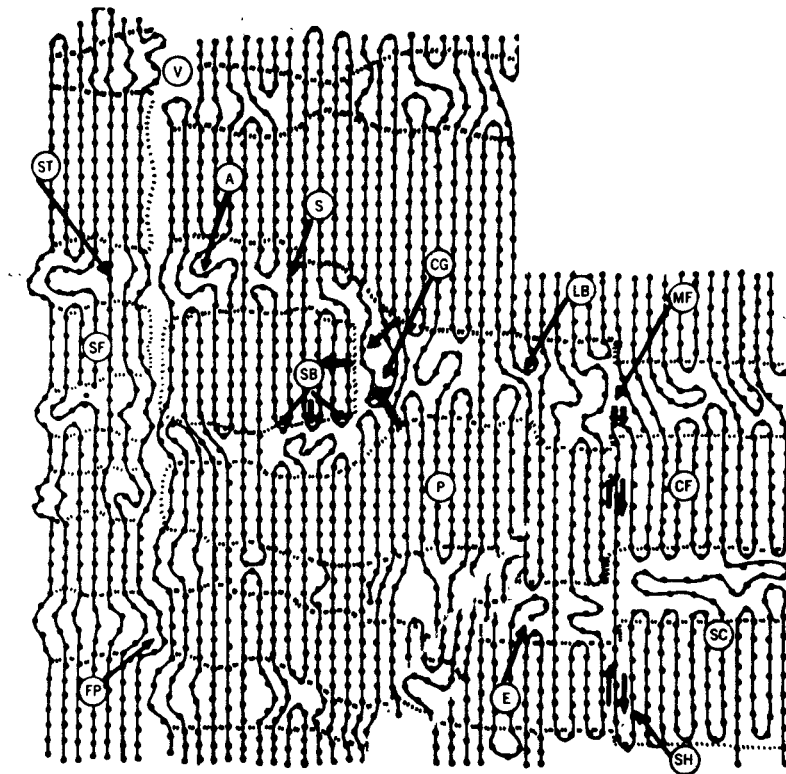


Fig. 5.9 A amorphous phase; CF clustered Fibrils; CG crystal growth in bulk; E end of a chain; FP four point diaagram; LB long backfolding; MF migrating fold; P paracrystalline lattice; S straight chains; SB short backfolding; SC single crystals; SF single fibrils (cold stretched); SM shearing region; ST Statton model; V voids (Van Turnhout, 1980). (with permission of Springer Verlag).

Equation (5.5) provides a good method for determining the jump frequency by measurement of dielectric loss. Such a technique has been used by Bueche (1962).

The assumption that the dipole is rigidly attached to the segment is not so restrictive because equation (5.5) still holds true, though the jump frequency now applies to the dipole rather than the segment. The jump frequency of the segment will be different. We

consider the molecule of poly-*m*-chlorostyrene (Bueche, 1962). The bond C-Cl is the dipole attached to the ring. The dipole moment which is directed from Cl to C can be resolved in two mutually perpendicular directions; one parallel to the chain and the other, perpendicular to it, along AB as shown in fig. (5.10). This latter component acts as though it is rigidly attached to the main chain. For this component to move the entire segment must move and equation (5.5) gives the frequency of jump. In other words the loss maximum observed at the glass transition temperature is related to the segmental motion. This kind of maximum is known as **α - loss peak** or **α -dispersion**.

Now consider the component perpendicular to AB. It can rotate more freely with the aromatic ring and this movement occurs more frequently than the rotation of a main chain segment. The loss maximum frequency will be correspondingly higher than that for the α -dispersion. This loss region is known as the **β -dispersion**.

The description presented so far assumes that the chain is made of segments that are freely jointed. If the segment is rigid or the molecule is short the molecular mass enters the picture. The α -dispersion frequency decreases with increasing molecular mass. In the case of stiff cellulose molecules, the α -dispersion frequency is found to depend upon the molecular mass. The rotation of units smaller than a side chain occurs even more frequently than the α or β dispersions, and the associated dielectric loss leads to so called **γ dispersion**, which occurs at a higher frequency than α - or β - dispersions. It is useful to recall that temperature may be used as a variable at constant frequency for the measurement of dielectric loss.

In view of eqs. (3.32) and (3.40) a dispersion that is observed at lower frequency with constant temperature corresponds to that at higher temperature at constant frequency. Hence, at constant frequency α -dispersion occurs at the highest temperature, β - and γ -dispersions occur at lower temperatures, in that order. δ -relaxation process occurs at even higher temperatures or lower f .

5.1.8 MOLECULAR STRUCTURE

In the following sections the dielectric properties of several polymers are discussed and it is more convenient to collect the molecular structure, as shown in Table 5.3.

5.2 NOMENCLATURE OF RELAXATION PROCESSES

The importance of morphology in interpreting dielectric data cannot be overstressed. For the sake of continuity we recall that measured dielectric loss as a function of temperature at constant frequency reveals the relaxation processes. Fig. 5.11¹⁵ is a

further description of the relation between the dielectric loss and morphology. Though the nomenclature described here was adopted by Hoffmann et. al. (1966) in describing the relaxation processes in poly(chlorotrifluoroethylene) (PCTFE), it is applicable for other polymers as well. For convenience sake, the temperature scale is normalized with respect to the melting point T_m . The polymer is assumed to be free of independent rotatable side groups and the dipoles are at right angles to the main chain.

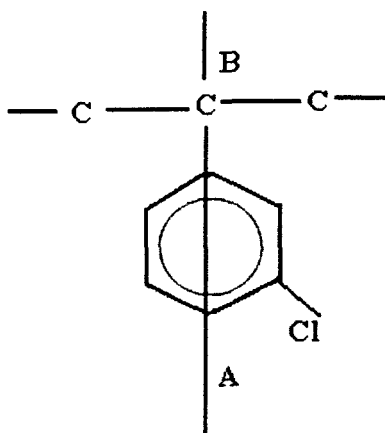


Fig. 5.10. Molecule of poly(m-chlorostyrene) used to define α - and β - dispersion (Bueche, 1962). (with permission of Inter science).

Further, the measurement frequency is assumed to be 1 Hz. The choice of this frequency as a reference is dictated by the fact that the frequency of molecular motion is 1 per second at T_m . As the temperature increases the peak shifts to higher frequencies for the same relaxation mechanism (Fig. 5.16 for example).

The highest temperature of interest is the melting point and at this temperature the relaxation is designated as α -relaxation. The processes at glass transition temperature in semi-crystalline and amorphous materials are designated as β -relaxation. Processes that occur at lower temperatures, possibly due to side groups or segmental polar molecules, are designated as γ - and δ -relaxations in order of decreasing temperature.

1. Single crystal slabs: The highest temperature peak in single crystals is the α_c -relaxation that occurs close to the melting point ($T/T_M \sim 0.9$) as shown in fig. (5.11 C). The relative heights of peaks shown are arbitrary. If the density of defects is low the peak will be higher than if the density is high. The subscript c merely reminds us that we are considering a crystalline phase. Since a single crystal is assumed to have no glass transition the β -relaxation is non-existent. The γ_c peak occurs at temperatures lower than T_G and may have one of the two components depending upon the defect density. The origin of the γ_c peak is possibly the defects wherein chains reorient themselves.

Table 5.3 Selected Molecular structure¹⁶ (Dissado and Fothergill, 1992).

Generic structure	Name (abbreviation)
$\begin{array}{c} \text{X} \quad \text{X} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{X} \quad \text{X} \end{array}$	$\text{X} = \text{H}$ polyethylene (PE) $\text{X} = \text{F}$ polytetrafluoroethylene (PTFE)
$\begin{array}{c} \text{H} \quad \text{X} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array}$	$\text{X} = \text{CH}_3$ polypropylene (PP) $\text{X} = \text{Cl}$ poly(vinyl chloride) (PVC) $\text{X} = \text{C}_6\text{H}_5$ polystyrene (PS) $\text{X} = \text{OCOCH}_3$ poly(vinyl acetate) (PVA)
$\begin{array}{c} \text{H} \quad \text{X} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{X} \end{array}$	$\text{X} = \text{Cl}$ poly(vinylidene chloride) (PVDC) $\text{X} = \text{F}$ poly(vinylidene fluoride) (PVDF) $\text{X} = \text{CH}_3$ polyisobutylene (butyl rubber)
$\begin{array}{c} \text{H} \quad \text{X} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Y} \end{array}$	$\text{X} = \text{CH}_3$ $\text{Y} = \text{COOCH}_3$ poly(methyl methacrylate) (PMMA)
$\begin{array}{c} \text{H} \quad \quad \text{X} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ -\text{CH}_2 \quad \text{CH}_2- \end{array}$	$\text{X} = \text{H}$ polybutadiene (BR) $\text{X} = \text{CH}_3$ polyisoprene (natural rubber)
$-(\text{CH}_2)_n-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\text{C}-$	$n = 2$ poly(ethylene terephthalate) (PET)
$-(\text{CH}_2)_n-\overset{\text{O}}{\parallel}\text{C}-\underset{\text{H}}{\text{N}}-$	$n = 5$ polyamide 6 (PA6, nylon 6) $n = 10$ polyamide 10 (PA10, nylon 10)
$-(\text{CH}_2)_n-\underset{\text{H}}{\text{N}}-\overset{\text{O}}{\parallel}\text{C}-(\text{CH}_2)_m-\overset{\text{O}}{\parallel}\text{C}-\underset{\text{H}}{\text{N}}-$	$m = 4, n = 6$, polvamide 6.6 (PA6.6, nylon 6,6)
$\text{C}_6\text{H}_4-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-$	polycarbonate (PC)
$\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-$	poly(ether ether ketone) PEEK

2. Completely amorphous phase (Fig. 5-11A): β -relaxation occurs above T_G ; the polymer is in a super cooled phase. In the glassy phase γ_a peaks are observed at temperatures lower than T_G . If the chemical structure is the same then γ_c and γ_a are likely to occur at the same temperature for moderately high frequencies. α -relaxation does not arise in the amorphous state while β -relaxation does not occur in single crystals.
3. Semi-crystalline (Fig. 5-11B): All the three relaxations may be observed; α_c peak occurs in the crystalline regions and β peak in amorphous regions. The γ peak is quite complicated and may occur both in the crystalline and amorphous regions.

5.3 NON-POLAR POLYMERS

We first consider the measured dielectric properties of selected non-polar materials.

5.3.1 POLYETHYLENE

Polyethylene is non-polar polymer that has a simple molecular structure. It is a thermoplastic, polyolefin with physical characteristics that can be controlled to a limited extent. The monomer is ethylene gas (C_2H_4) and additional polymerization yields a polymer that is linear with a C-C carbon chain as the backbone. The carbon atoms make an angle of about 107° with each other, the entire carbon chain lying in the same plane. There are no independently rotatable side groups.

Low density polythene (LDPE) is produced at pressures as high as 150 MPa (1500 atmospheres) with appropriate safe guards to prevent explosion due to exothermic reactions. Recent advances are to lower the pressure to 600 atmospheres. The process yields a single chain polymer with short branches of a few carbon atoms along the main chain. Molecular weight is typically 20000-50000 and the number of monomers in a chain can be as large as 10,000. It is highly resistant to alkalis and acids. It does not have any solvent at room temperature but at $100^\circ C$ there are a number of organic solvents in which it dissolves. As the solution cools polythene precipitates out.

LDPE is susceptible to sunlight and cannot be used out doors unless additives are used. It has moderate mechanical strength, but its cheapness is an attractive feature for low voltage cable insulation. To improve the electrical characteristics, copolymers with 5% of 1-butene ($CH_2=CH-CH_2-CH_3$) or cross linked polyethylene is used for electrical cables.

High density polythene (HDPE) is more crystalline, has a higher density, has a higher melting point, is more resistant to chemicals and is mechanically stronger. The physical characteristics are shown in Table 5.4.

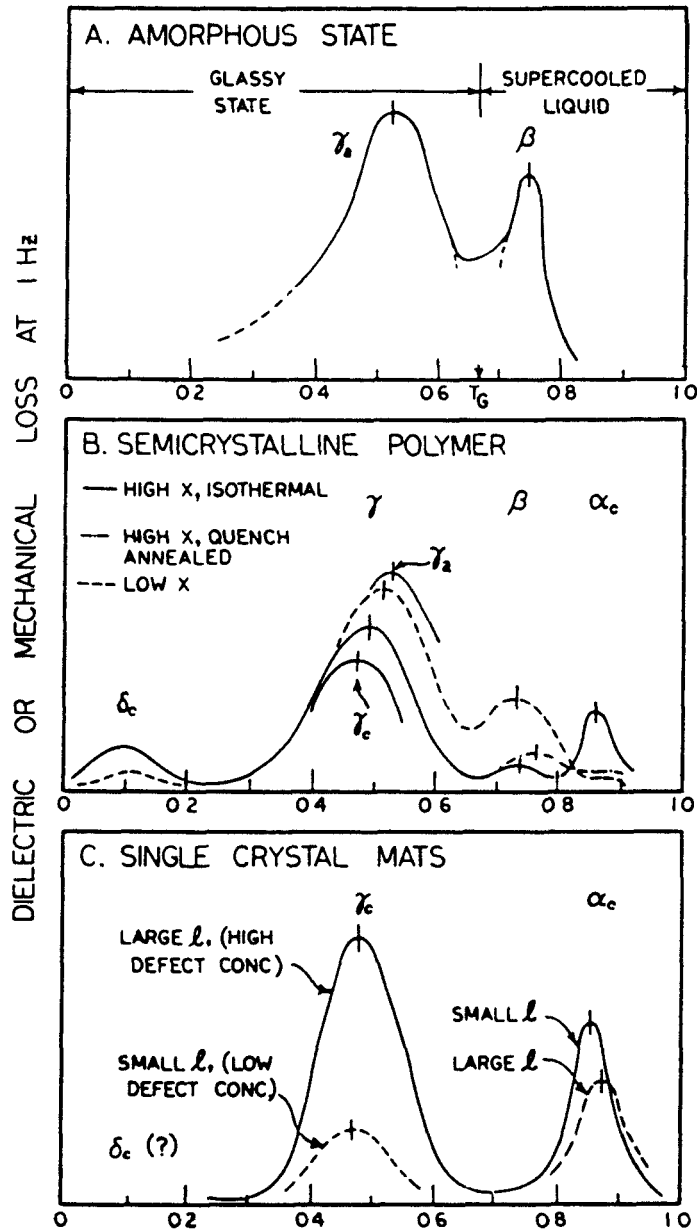


Fig. 5.11 Nomenclature for relaxation processes. T_m is the melting temperature, T_g the glass transition temperature, l the lamella thickness, x the mass fraction of crystallization (Hoffmann et. al., 1966, with permission of J. Poly. Sci.)

The glass transition temperature is -125°C , quite low because (i) strong intermolecular cohesive forces are absent (ii) the atom bonding with carbon is hydrogen which has the lowest mass. Linear polyethylene is highly crystalline (90%) though branching reduces it to 40%. Branching introduces irregularity to the molecular structure and reduces the

ability of the molecules to pack closely together. The ability to crystallize is correspondingly reduced.

Table 5.4
Physical Properties of Polyethylene.

Property	Low density PE	High Density PE
Melting point (°C)	110-125	144-150
Density (kg/m ³)	910-920	965
T _g (°C)	-	-125
Crystallinity (%)	40	90

The dielectric constants of low density and high density polyethylene at low frequencies are 2.286 and 2.355 respectively. A comparison with Fig. 2.4¹⁷ with calculated values shows a reasonable agreement. The Clausius-Mosotti factor is a linear function of density and Barrie et. al.¹⁸ find from their measurements that the expression

$$\frac{\varepsilon - 1}{\varepsilon + 2} = k\rho \quad (5.6)$$

where k is a constant having a value of $3.24 \times 10^3 \text{ (kg/m}^3\text{)}^{-1}$ and ρ the density holds true.

Buckingham and Reddish¹⁹, Barrie, Buckingham and Reddish (1966) and Reddish²⁰ have measured the loss factor. The loss angle of about 30 μ rad at 1 kHz and 12 μ rad at 5 kHz, at very low temperatures is independent of frequency from 4.24 K to 80 K.

Fig. 5.12 shows the measured loss data in medium density polyethylene at various temperatures and separation of the loss into two nearly equal mechanisms, β and γ mechanisms. The high temperature β -process (peak 10°C) and the low temperature γ -process (peak -90°C) is evident in all cases; the peak of the β dispersion is clearly seen at 10°C (fig. d). There is evidence that the α - process has an onset temperature at 30-40°C (fig. e) and from other studies it is known that this process occurs at lower frequencies at 80°C.

Polyethylene is a dielectric with low loss angle covering a five decade frequency scale as measured by Reddish at room temperature. In this frequency range the dielectric loss is reasonably independent of temperature. Jonscher considers this as evidence for the fact that the index n , in his empirical loss equation (4.1), is approximately equal to one, independent of frequency. In contrast the loss angle varies with temperature more

vigorously at lower temperatures (fig. 5.12 b) due to change in structure. We recall that the glass transition temperature of polyethylene is 160 K, which lies in the region where the fluctuations are observed. We should not overlook the fact that this is the region of interest from the behavior point of view, and Jonscher's equation does not throw much light on this aspect.

A brief explanation of the reasons for observing three dispersions in non-polar polyethylene is in order. Theoretically a non-polar polymer with linear chain should show only the α -dispersion since the only motion that can occur is due to the main chain at the glass transition temperature. However the LDPE has branches of carbon atoms, about 50 per molecule, distributed along the chain at intervals of about 100 main units. Branches of approximately the main chain length may also exist at intervals of a few main chain lengths. The degree of chain branching changes rapidly with density and comparing results obtained by different experiments is difficult because the sample used may not have exactly the same morphology. It has also been suggested that the β -dispersion is not due to the branches but due to the glass transition of the amorphous regions. The γ -process involves at least four CH_2 molecules that may participate in a crankshaft movement in the amorphous region.

During the 1960's the use of polyethylene in submarine cables spurred research into dielectric loss mechanisms, in particular on the effects of moisture and oxidation. Micro-droplets of water in PE cause a dielectric loss in proportion to the amount of water absorbed. With a water content of 190 ppm the dissipation factor ($\tan \delta$) increases to 1.5×10^{-4} at 10 MHz²¹. The origin of the loss is due to Maxwell-Wagner dispersion which occurs due to the motion of impurity ions in the water molecule.

Dielectric loss in oxidized PE occurs at a frequency of ~ 10 GHz and this is considered to be an intrinsic property of PE, due to localized dipolar motion in the amorphous phase. The oxidation of PE introduces polar carbonyl groups which are short and rigidly attached to the main chain. Any movement of the dipole is associated with the motion of the chain and the polar molecule acts as a probe to observe the natural motion of the chain.

The results in polyethylene may be summarized as follows:

1. Three loss regions are observed in polyethylene; the exact temperature and frequency depends upon the morphology and impurity in the samples.
2. The α -dispersion occurs at high temperature $\sim 80^\circ\text{C}$ at 100 Hz, these values changing with crystallinity. It is probably due to chain motion in the crystalline region.

3. The β -dispersion occurs at $\sim 10^\circ\text{C}$ and 1 kHz, probably due to branches attached to the main chain. The magnitude of the loss depends upon the number of side groups attached. The temperature at which relaxation occurs is not affected, however, by the length or number of side groups since the side groups themselves do not interact.
4. The γ -dispersion occurs at low temperatures, possibly due to the crankshaft motion in the amorphous regions.

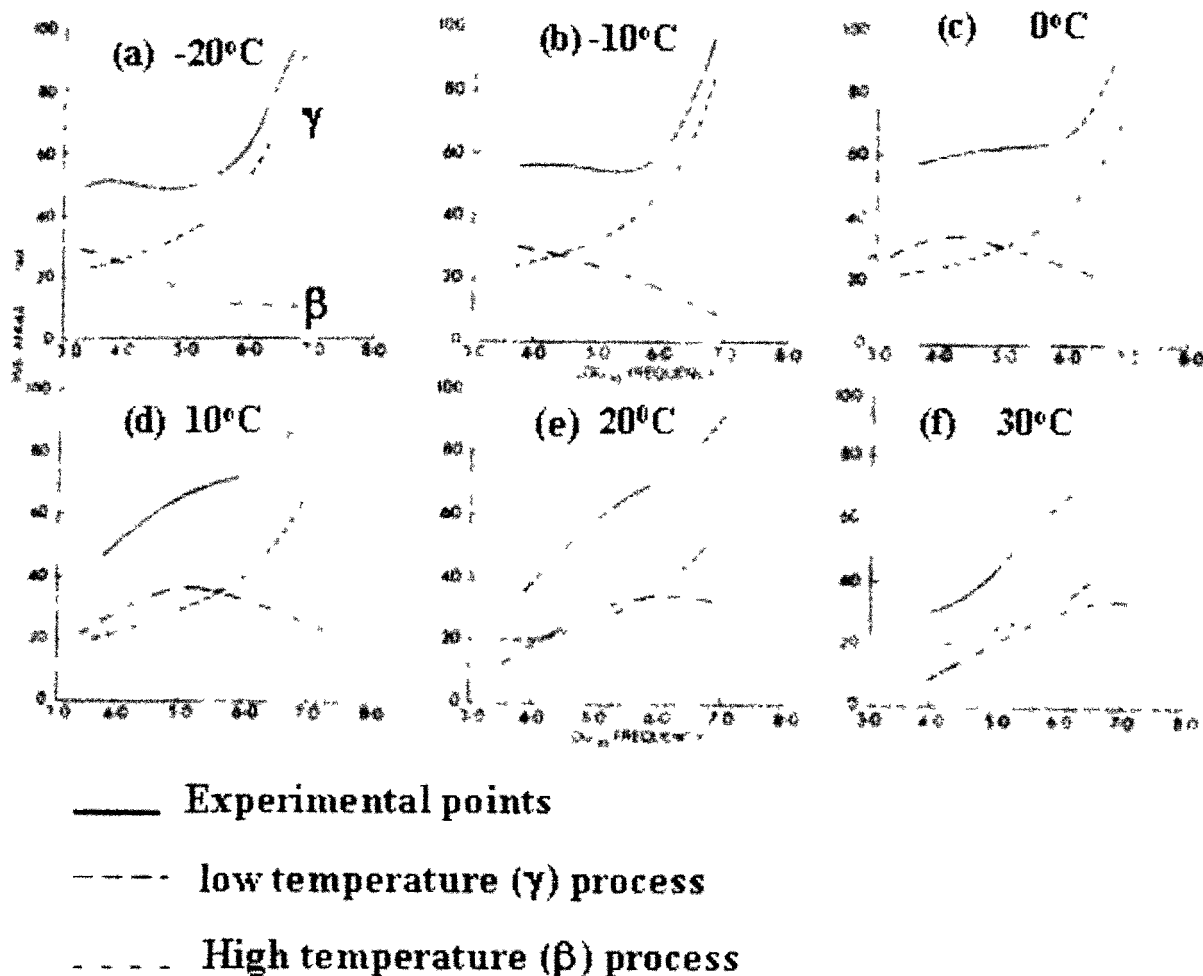


Fig. 5.12 Relative contributions to loss angle of the two relaxation processes in medium density polyethylene (Barrie et. al., 1966, with permission of IEE).

5.3.2 POLY(TETRAFLUOROETHYLENE)

Poly(tetrafluoroethylene), abbreviated as PTFE, is a non-polar polymer that has a chemical structure as simple as polyethylene except that all the hydrogen atoms are replaced with fluorine atoms (Table 5.3). The monomer is a gas with a boiling point of -76°C . The polymer has a highly regular helical structure with a linear main chain and no branches. This is due to the fact that the C-F bonds are quite strong and they are unlikely

to be broken during polymerization. It is also highly crystalline (upto 93-98%) and has a melting point of 330°C. It is highly resistant to chemicals and has a low coefficient of friction. It has a low dielectric constant, large acoustic absorption, very good compatibility with biological tissues and high vapor transmission rate. Highly porous PTFE²² (fig. 5-13) is commercially available in various grades and has demonstrated high surface charge stability even up to 300°C. Recent progress includes development of amorphous grades (Teflon® AF) that have 95% optical transmission in the range of 400-nm to 2000 nm. Since this grade does not absorb light it does not deteriorate when exposed to light. It has a low dielectric constant of ~1.9.

The early results of Krum and Muller²³ over a wide temperature range of 83-623 K using frequencies of 1-316kHz, also exhibited the three dispersions like polyethylene. However more recent investigations²⁴ have led to the conclusion that the α - and β -relaxations are possibly due to polar groups as impurities and not representative of the polymer. The low temperature γ -relaxation at ~ 194 K is the characteristic of the material, attributed to motions of short chain segments in the amorphous regions. The Arrhenius relationship

$$\omega_{\max} = A \exp - \frac{\varepsilon_a}{kT} \quad (5.7)$$

is found to hold true for this relaxation in the temperature range of 160-225 K with an activation energy of 0.7 eV.

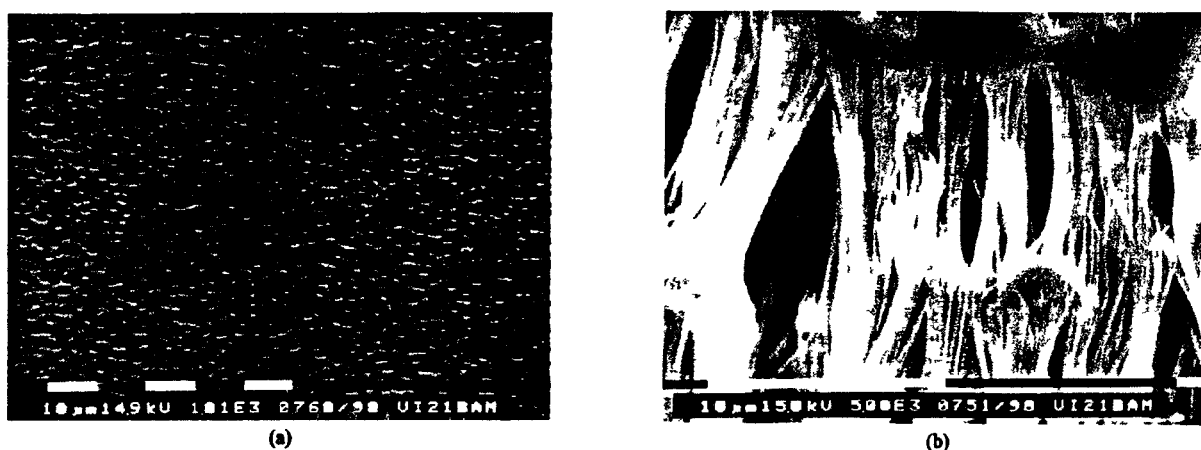


Fig 5.13 Scanning electron micrograph of (a) non-porous and (b) porous PTFE films taken at magnifications of 1010 and 5000, respectively (Xia et. al. 1999, with permission of J. Phys. D: Appl. Phys.)

High pressure has a pronounced influence on the complex dielectric constant, ϵ^* , due to the fact that internal motions are restricted due to decreased volume. Fig. 5-14 shows the dissipation factor ($\tan\delta$) at constant temperature with pressure as the parameter²⁵. With increasing pressure the activation energy increases from 0.7 eV at 1 bar to 0.92 eV at 2500 bar.

Though pure Teflon shows only γ -relaxation at low temperatures the effect of impurities has been demonstrated by immersing PTFE in both polar and non-polar liquids. While non-polar carbon tetrachloride did not introduce any significant change, polar liquids like chloroform and fluorocarbon-113 increased the maximum for $\tan \delta$ at 1 kHz. Further the polar molecules introduced an additional large loss peak at ~ 50 K. These changes were also associated with the shift of the γ -peak to lower temperatures²⁶.

5.4 POLAR POLYMERS

Replacement of one or several hydrogen atoms in CH_4 renders the molecule polar. As a rule the various characteristics like thermal stability, mechanical strength, etc. are achieved by suitable substitutions and the process inevitably imparts a dipole moment to the molecule. There are many more polar polymers than non-polar. Polymers possess a dipole moment due to the presence of one or several types of polar bonds located in the polymer structure in such a way that the dipole moment of the bonds do not neutralize each other. The polar group may be situated in the main chain, a side group or attached to an aromatic ring. In the following we discuss the relaxation phenomena in selected polymers.

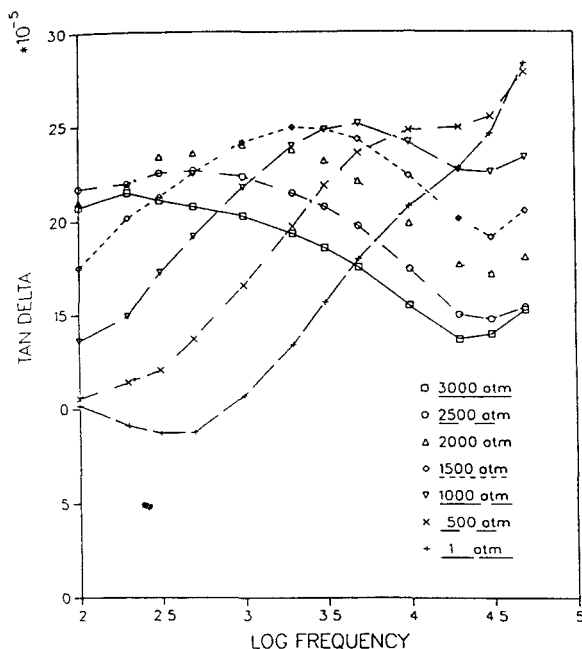


Fig. 5.14 The effect of pressure on the γ - relaxation in PTFE at a constant temperature of 212 K (Starkweather et. al. 1992). (with permission of A. Chem. Soc.)

5.4.1 POLYPROPYLENE

Polypropylene is a mildly polar hydrocarbon that has a low density of 910-920 kg/m³. Structurally it is related to polyethylene with the hydrogen atom linked to alternate carbon atoms replaced with CH₃. It can be prepared in isotactic, syndiotactic or atactic forms (fig. 5-5). The isotactic form melts at 208°C and has high crystallinity. The molecules are essentially linear and form a helical configuration. It has high stiffness and tensile strength due to its high crystallinity. Though it is highly resistant to chemicals at room temperatures it dissolves in aromatic and chlorinated hydrocarbons near its melting point. The evolution of spherulites in i-PP from the melt is shown in fig. 5-15 (Kim, 2000). Crystallization starts at 130°C and ends at 118°C. In the s-PP, on the other hand, crystallization begins only at 110° C and saturates at 100°C.

Polymer crystallization is generally affected by the probability that a molecule is able to form a crystalline arrangement with the neighbors. This probability depends upon the length of the repeating unit. A long and uniform length of main chain acts as a generation center of a spherulite. The i-PP has a ratio of Molecular weight to molecular number of 4-12, whereas s-PP has a ratio of 2. This makes the packing efficiency in s-PP greater giving it a good stereochemically symmetrical molecular structure, with a zig-zag configuration of the methyl groups (CH₃) along the main chain (Kim, 2000).

Kramer and Heif²⁷ have measured ϵ' and ϵ'' in polypropylene over a temperature range of -75°C-140°C and a frequency range of 0.15 kHz-140°C. The samples were mostly isotactic with 2-3% atactic, having a crystallinity of 5%. The molecular mass is 30000. The dielectric constant increases as the temperature is increased from -75°C and reaches a maximum at 25°C and for further increase, there is change of slope of ϵ' - 1/T curve. This aspect has been briefly touched upon earlier in this chapter. We will consider it in greater detail in connection with PVC.

The loss angle shows both α - and β -relaxations. The β -relaxation occurs 20°C ($T_g \sim 0^\circ\text{C}$) at 0.15kHz and the relaxation temperature increases to 60°C at 300 kHz as the theory requires. The α -relaxation occurs in the 100-140°C range. The maximum frequency for both absorptions follows the **Arrhenius law**

$$f_{\max} = A \exp\left(-\frac{W}{kT}\right) \quad (5.8)$$

where the activation energy W is 6.5eV and 1.21eV for α - and β -relaxation respectively. The relatively large energy observed is not unusual for polymers with a molecular mass

of several thousand. A simplified explanation of this phenomenon is given below [Daniel, 1967].

Proceeding on the assumption that the jump frequency ϕ is thermally activated we can express that

$$\phi = \phi_0 \exp\left(-\frac{W}{kT}\right) \quad (5.9)$$

where the pre-exponential factor ϕ_0 is much less sensitive to the temperature than the exponential that contains the critical energy for a jump, W . If the temperature is very high the exponential factor will almost be equal to unity and ϕ_0 is approximately equal to ϕ .

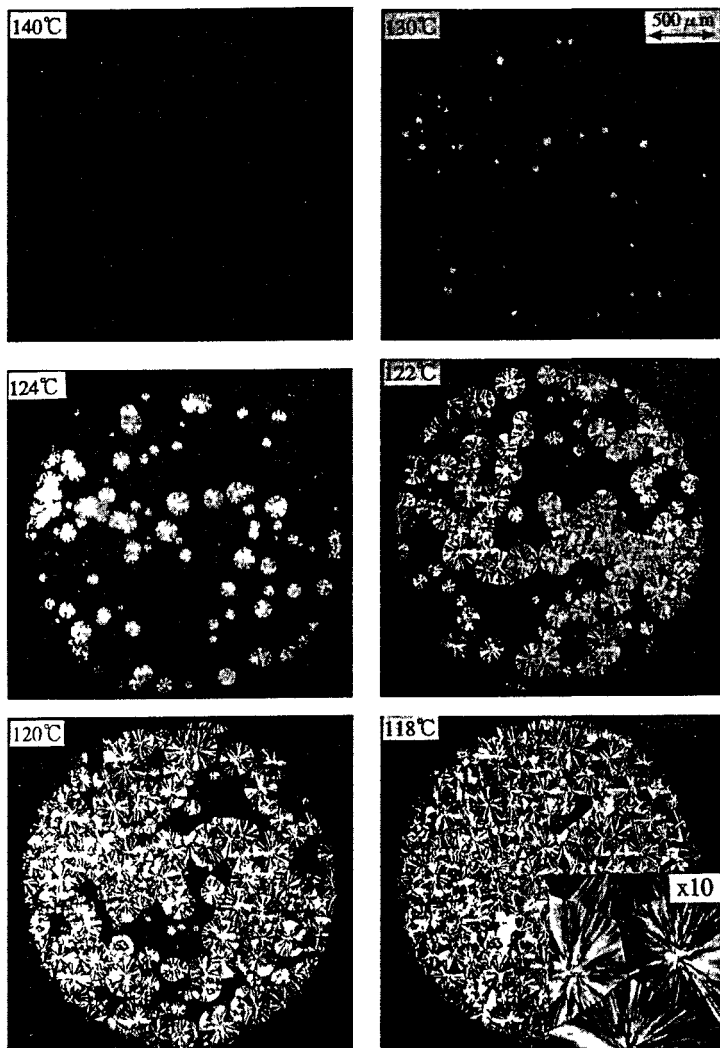


Fig. 5.15 Growth of Spherulites in i-PP during cooling process (Kim, 2000, with permission of J. Phys. D: Appl. Phys.)

Now, the viscosity of a polymer depends upon many factors including the jump frequency and only ϕ appears to be temperature sensitive. Since the viscosity is high when ϕ is low, the consequence is that W is large near α -relaxation temperature. For most polymers the energy is close to 0.5 eV and at glass transition temperature it could be as large as 10 eV. In PMMA, for example, a critical energy as high as 12 eV has been reported.

The glass transition temperature of polypropylene is -18°C and melting temperature is $\sim 170^{\circ}\text{C}$. It is a slightly polar semicrystalline polymer. The α -relaxation occurs at a much higher temperature relative to the glass transition temperature. In an attempt to explain the discrepancy it has been suggested (Work, et. al., 1964) that the observed high temperature relaxation is possibly due to oxidation products and impurities.

Work, McCammon and Saba²⁸ have measured ϵ'' in highly purified atactic polypropylene as shown in fig. 5.16 in the temperature range of 4-300 K at each of several frequencies in the range 100-20 kHz. The ϵ'' peak occurs in the temperature range of 275-295K which is much closer to the glass transition temperature of their sample, 267K. Using the Cole-Cole plot and from the dielectric decrement obtained, the dipole moment of a polypropylene chain unit has been determined as 0.05 D. Work, et. al have not commented on the origin of this dipole moment.

Jonscher has evaluated values for the index in his formula (4.1) as $m = 0.37$ and $n = 0.24$ from the loss data of Work et. al. Low frequency loss factors in isotactic PP has been reported by Banford et. al.²⁹

The relaxation properties of this polymer may be summarized as follows:

1. A high temperature α -relaxation around 100°C due to reorientation of main chain in the crystalline regions
2. A lower temperature β -relaxation at $\sim 10^{\circ}\text{C}$ in the amorphous regions.

5.4.2 POLY(VINYL CHLORIDE)

Poly(vinyl chloride), abbreviated as PVC, is one of the cheapest and extensively used polymers. The monomer, vinyl chloride, boils at 259 K and therefore it is a gas at room temperature. Hence polymerization is carried out in pressure reactors. PVC has low crystallinity ($\sim 10\%$) and the molecules are either linear or slightly branched. Normal PVC has a molecular weight of 60,000-150,000. The molecular structure is only partially syndiotactic and lacks complete regularity with low crystallinity. The material is hard to process unless **plasticizers** are used; plasticizers lower the glass transition temperature from a value of 81°C for the unplasticized material. PVC has a melting

point of 310°C decomposing before the melting point is reached and it is not thermally stable even at moderately high temperature. Stabilizers such as Zinc octoate, sodium carbonate, certain salts of calcium, barium or lead, organo-tin compounds, epoxidised vegetable oils are used to minimize decomposition at high temperature and exposure to sun light.

The chlorine content of PVC is 56.7% by weight and can be further increased by dissolving it in a solvent such as chlorobenzene and chlorinating at temperature ~100°C. The resulting polymer is called **chlorinated PVC** (CPVC) with chlorine content increasing in the range 60-65%. During chlorination, the chlorine replaces the hydrogen atoms in CH₂ units rather than in the CH—Cl units. Chlorination increases the chemical resistance but thermal resistance is reduced.

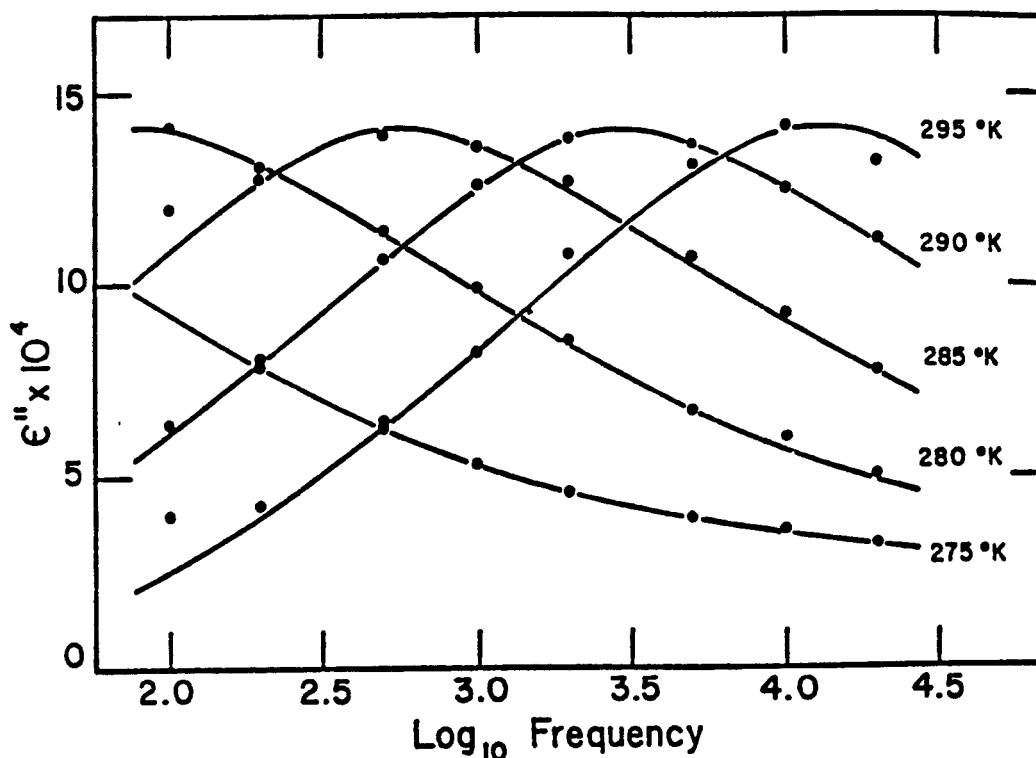


Fig 5.16 Dielectric loss factor of polypropylene (works et. Al., 1964). (with permission of A. Chem. Soc.).

Ishida³⁰ has measured the dielectric constant and loss in PVC and Deutsch et. al.³¹ have further extended the study to chlorinated PVC using both electrical bridges and polarization techniques. The latter consists of poling the material at an appropriate electric field and measuring both polarization and depolarization currents as a function of time (see ch. 6). These measurements are carried out isothermally and the correction

of ϵ'' due to contribution from conduction currents (eq. 3.8) applied to the polarization currents. The time domain current is transformed to frequency domain to yield the loss factor at lower frequencies.

Fig. (5.17) shows the dielectric properties of PVC at higher temperatures. The observed maximum in ϵ'' is due to the β - relaxation. In this temperature range the absorption becomes stronger as the temperature increases, the frequency of the maximum ϵ'' shifting to higher values.

Fig. (5.18) shows similar data at lower temperatures and the peak here is attributed to the γ -relaxation. It is noted that the nomenclature which is adopted here is due to Bur (1984) because the α -absorption, in fact corresponds to the melting point. We will refer to this value while another polymer of the same family, poly(vinyl fluoride) is discussed. Fig. 5.19 shows ϵ' presented as a function of temperature at various constant frequencies³². The dielectric constant at various temperatures is shown in Table 5.5. The repeating unit of PVC has a dipole moment of 1.1 D. The sharp rise in ϵ_s at 354 K is identified as a transition temperature at the Curie point as discussed in section 2.7. At temperatures higher than T_c , the dielectric constant decreases according to $1+3T_c/(T-T_c)$ as the Debye theory requires.

The transition becomes steeper and reaches higher values as the frequency is reduced. A structural change could explain the existence of a critical temperature. The implication is that the polymer has structural order above T_c and disorder below T_c , the transition occurring due to the motion of rod-like short segments. In the disordered state that exists below T_c alternate chlorine sides are directed in opposite directions, the dipoles being at right angles to the rod segment. At higher temperatures the rods rotate co-operatively to align the dipoles. The rotational motion increases the dipole moment leading to a higher dielectric constant. The number of repeating units N_u in each moving segment depends on the temperature as shown in Table 5.5. With increasing temperature, the number of units decreases explaining the peak of the dielectric constant at T_c .

The number of repeating units in a moving segment is calculated, for a first approximation, as follows. The Onsager equation for the dielectric constant is given as:

$$(\epsilon_s - \epsilon_\infty) = \frac{3\epsilon_s}{2\epsilon_s + \epsilon_\infty} \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \frac{N\mu_v^2}{3\epsilon_0 kT} \quad (2.84)$$

where N is the number of repeat units per m^3 and μ_v is the moment of a dipole in vacuum. Applying the relationship:

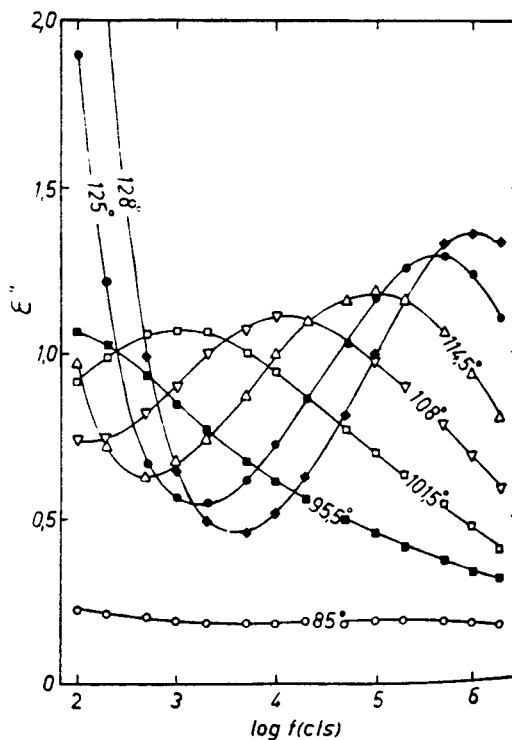
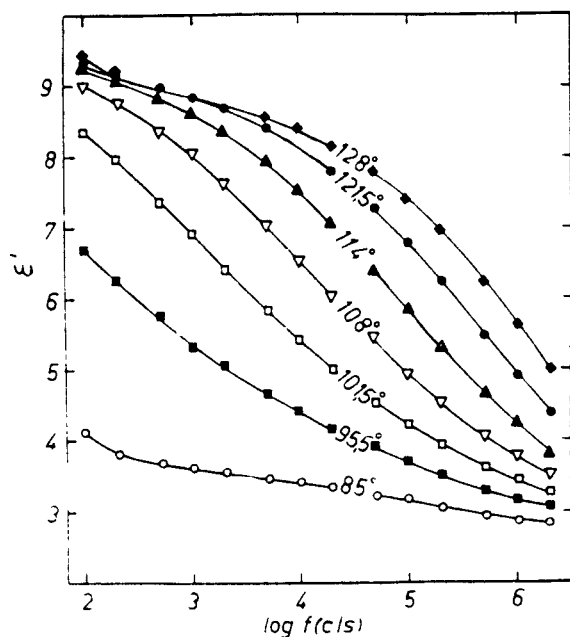


Fig. 5.17 Dielectric constant and loss factor of PVC at high temperatures showing β -absorption.(Ishida, 1960, with permission of Dr. Dietrich Steinkopff Verlag, Darmstadt, Germany).

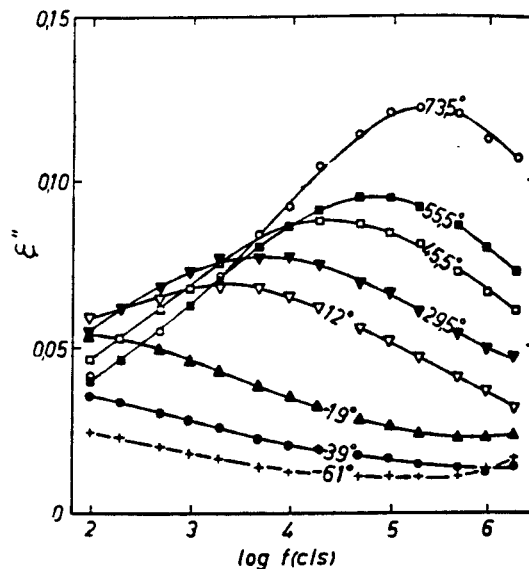
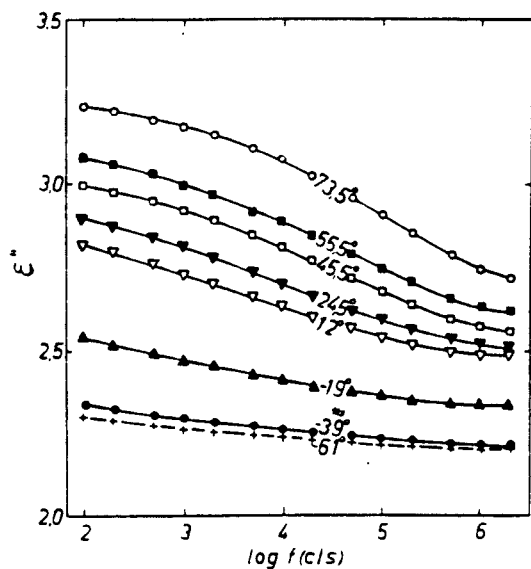


Fig. 5.18 low temperature γ -relaxation in PVC (Ishida, 1960). (With permission of Dr. Dietrich Steinkopff Verlag, Darmstadt, Germany)

$$N = N_A \frac{\rho}{M}$$

where N_A is the Avagadro number (6.06×10^{23} /mole), ρ the density (1400 kg/m^3), M the molecular mass ($62.5 \times 10^{-3} \text{ kg/mole}$). Substitution gives $N = 1.36 \times 10^{28} / \text{m}^3$. Several dipoles move co-operatively and let n be the number of repeat units that move during relaxation.

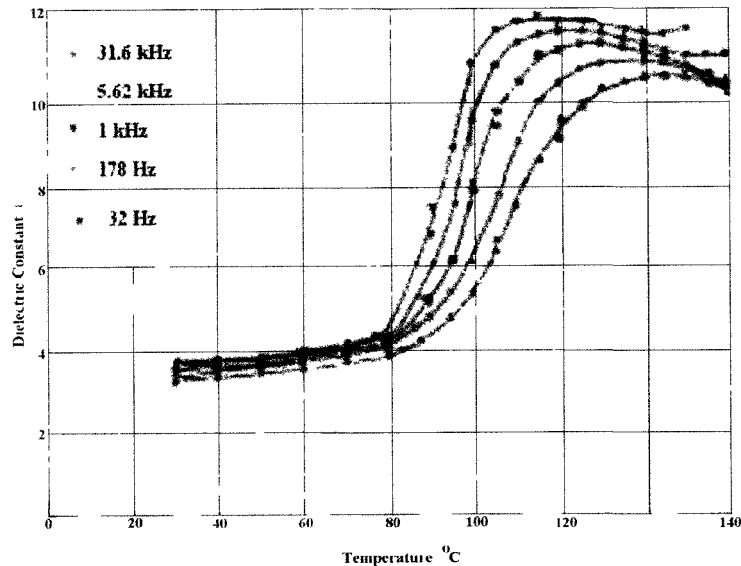


Fig. 5.19 Dielectric constant of chlorinated PVC in alternating fields, 56% Cl. (Reddish, 1966). (with permission of J. Poly. Sci.)

Table 5.5

Dielectric properties of Chlorinated PVC (Reddish, 1966)

T (K)	ϵ_s	No. of repeat units (N_u)	$\mu^2 N_u (D^2)^*$
425	11	2.38	3.14
400	12	2.48	3.27
375	15	3.02	3.98
370	16.2	3.23	4.26
365	18.5	3.68	4.38
360	22.2	4.44	5.85
354.3	37	7.52	9.91

* $D=1$ Debye unit= $3.33 \times 10^{-30} \text{ C m}$

Then N/n is the number of motional units and $\mu_v n$ is the dipole moment of a motional unit. Substituting these values, the Onsager's equation now becomes:

$$n\mu_v^2 = \frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s} \left(\frac{3}{\varepsilon_\infty + 2} \right)^2 \frac{\varepsilon_0 kT}{N} \quad (5.10)$$

The dipole moment in a vacuum is related to the moment of the dipole (1.1D) according to

$$\mu^2 = \left(\frac{\varepsilon_\infty + 2}{3} \right)^2 \mu_v^2 \quad (5.11)$$

Substituting equation (5.11) into (5.10) results in

$$n = \frac{(\varepsilon_s - \varepsilon_\infty)}{3\varepsilon_s} \frac{(2\varepsilon_s + \varepsilon_\infty)}{\mu^2} \frac{3\varepsilon_0 kT}{N} \quad (5.12)$$

We collect the values to calculate n :

$T = 425$ K, $\varepsilon_s = 11$ (from top row of Table 5.5), $\mu = 1.1 \times 3.3 \times 10^{-30}$ C m, $N = 1.36 \times 10^{28}$ /m³, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, $k = 1.38 \times 10^{-23}$ J/K. We get $n = 2.38$. From Table 5.5 we see that the number of co-operating units increase as T_c is approached.

The motion of the dipoles changes the internal field and at each temperature a finite time is required for the equilibrium state to be established. At T_c this time is of the order of several thousand seconds, which explains the increase of the dielectric constant with decreasing frequency at T_c (fig. 5.19).

Increasing the chlorine content of PVC has been found to decrease the dielectric constant and loss factor. The second chlorine atom attaches to the same carbon atom as the first, neutralizing the dipole moment, and this has the effect of neutralizing some of the dipole moment. Consequently both ε' and ε'' are reduced, the reduction being largest for the highest chlorine content (69.1%). The peak is also shifted to higher temperatures.

We summarize the results in PVC as follows;

1. At T_g the dielectric constant exhibits a disorder-order transition involving unrestricted rotation, in place of restricted rotation, of rod like segments of chain units. The dipoles are perpendicular to the main chain (Bur, 1985).
2. The dielectric constant at this temperature shows a peak at audio frequencies. The change of dielectric constant is time dependent, reaching a discontinuity at 10^{-4} Hz.
3. Chlorination of PVC results in reduced maximum of ε'' and ε' at 1 kHz.

5.4.3 POLYCHLOROTRIFLUOROETHYLENE

Polytrifluoroethylene, abbreviated as PCTFE, with the trade name of KEL-F 300 has density in the range of 2090-2160 kg/m³. The number average molecular weight is approximately 415,000 corresponding to a number average chain length of 900 nm. The glass transition temperature is in the range of 40-59°C and crystals have a melting point of ~200°C.

PCTFE, like polyethylene, does not possess any independently rotatable side groups and any observed relaxation process is, in some way, related to the motion of parts or of the entire chain. It has a dipole unit on each monomer chain and the dielectric properties have been studied quite extensively. PCTFE exhibits a wide range of crystallinity (12-80 %) depending upon the method of preparation. By changing the crystallinity and measuring the dielectric properties, Hoffmann et. al. (1966) identified the relaxation mechanisms with the crystalline or amorphous regions.

A. MORPHOLOGICAL DETAILS

Scott, et. al.³³ have measured the dielectric properties of this polymer in the frequency range of 0.1-10¹⁰ Hz. and an extensive discussion of these studies have been published by Hoffmann et. al (1966). We follow the presentation of these authors because of the thorough treatment. The data were obtained in three different samples which had varying degrees of crystallinity.

1. Bulk polymer crystallized from the melt with slow cooling: The sample had 80% crystallinity. The growth of spherulites in bulk crystallized polymers has already been discussed and PCTFE behaves entirely typically in this respect. Each spherulite starts from a nucleation center with the plate like lamallae having a thickness of 30-80 nm depending on the temperature of crystallization and time of annealing. Higher temperatures and longer annealing result in thicker samples. The lamallae has a chain folded structure with nearly regular folds and adjacent reentry.

These characteristics mostly, though not entirely, determine the dielectric properties. The inter-lamaellar region is filled with low molecular weight material that has failed to crystallize. It has been established that only molecular chains that have a length greater than a critical length undergo chain folding; shorter molecules are excluded from the crystallization mechanism. The short molecules grow outside the lamallae as extended chains. The crystalline region therefore has two separate regions: 1. Chain folded lamallae. 2. Extended-chain region. The existence of these two regions has also been confirmed in polyethylene (Hoffmann et. al., 1966).

2. Bulk polymer crystallized from melt by quench cooling: This method yields bulk polymer having low crystallinity of 12% and 44%. Since a large number of nucleation centers are active only very small crystallites are formed in the majority explaining the low crystallinity. Larger crystallites give the polymer higher crystallinity. It is noted that small crystallites are not formed in polyethylene due to crystallization kinetics. The amorphous regions consist of numerous chains interlinked like cooked spaghetti.

3. Quench crystallized and annealed samples have intermediate crystallinity of 73%. Both the samples, 73% and 80% crystalline, have inter-lamellar links. Such links exist in crystallized polyethylene too. The inter-lamellar links decrease crystallinity and therefore in highly crystallized samples the number of these links is small. Annealing seems to decrease the number of these links.

B. THE α -RELAXATION

Fig. 5.20 shows the dielectric loss factor plotted as a function of frequency at various temperatures for a sample with 80% crystallinity. The figure also includes the $\epsilon' - \log f$ data. The details at low frequency and higher temperatures ($\geq 150^\circ\text{C}$) are shown in fig. 5-21. The α_c -relaxation peak at 150°C ($T = 0.86 T_M$) can be seen clearly at 1 Hz. Note the shift of the peak to a higher frequency at 175°C . The α_c -relaxation is not evident at the highest temperature of 200°C because the peak has moved beyond the highest frequency available. Another distinct behavior observed at this temperature is the onset of dc conductivity at the lowest frequencies. Hoffmann et. al. (1966) provide evidence to suggest that the loss is associated with the surface of the crystal rather than the interior. Using equation (5.8) the activation energy is determined as 3.47 ± 0.43 eV. The relaxation is attributed to overlapping mechanisms; motion of chain folds and translations of chains in the interior. For long chains, twisting of chains is also a contributing factor.

C. THE β -RELAXATION

The β -relaxation occurs in samples with lower crystallinity (44% and 73%). A peak is observed in the $\epsilon'' - T$ curve at a temperature of 125°C . This temperature is much higher than T_G (~ 50 - 59°C) for both samples, but lower than T_M .

Do we assign the peak to α_c -loss in the crystalline region, or to β -loss? Such questions frequently arise in dielectric studies in interpreting experimental data. Since the peak value of ϵ'' increases with decreasing crystallinity it is reasonable to assume that the loss is related to the amorphous regions. Further the α -, β -, γ -relaxations are closely interlinked with the distribution of relaxation times discussed in ch. 4 and the shape of

the ϵ'' - $\log \omega$ curves, which is dependent on this distribution, provides complementary data about the nature of the loss mechanisms.

By plotting f_{max} as a function of $1/T$ the activation energy may be determined according to equation (5.8). According to Davidson and Cole³⁴ the mean relaxation time in amorphous materials is given by

$$\tau_m = \frac{1}{\omega_p} = \tau_0 e^{\frac{w_r}{k(T-T_c)}} \quad (5.13)$$

where τ_0 and T_c are constants. The viscosity of liquids is given by the equation of the same type

$$\eta_g = \eta_0 e^{\frac{w_g}{k(T-T_c)}} \quad (5.14)$$

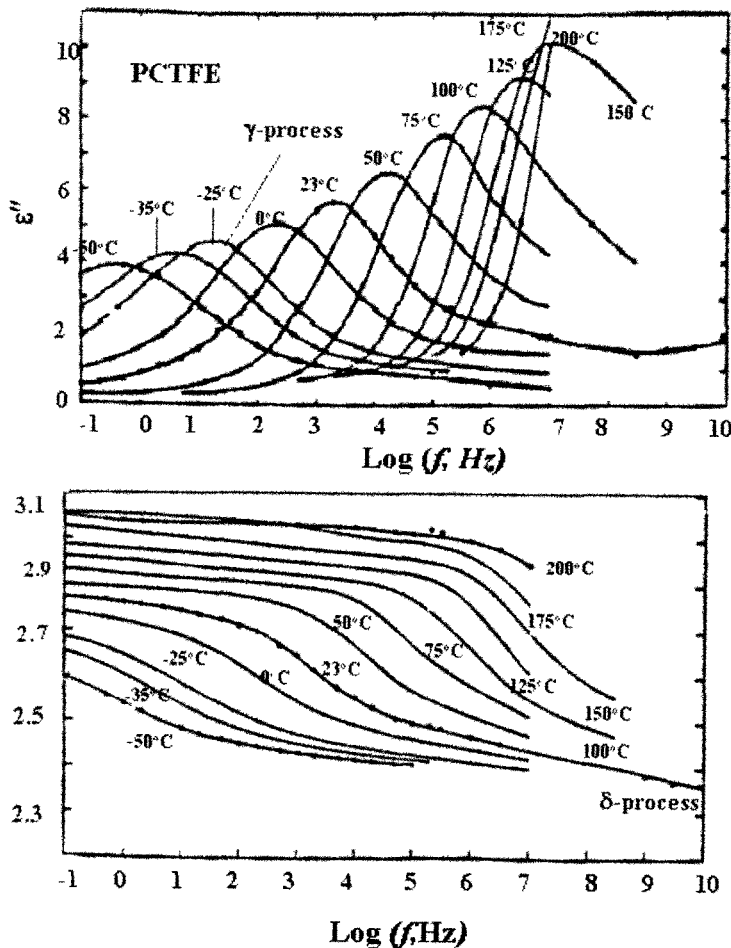


Fig. 5.20 Loss factor and dielectric constant of 80% crystalline PCTFE at various temperatures (Scott et al., 1962). (With permission of National Bureau of Standards, Washington D. C.)

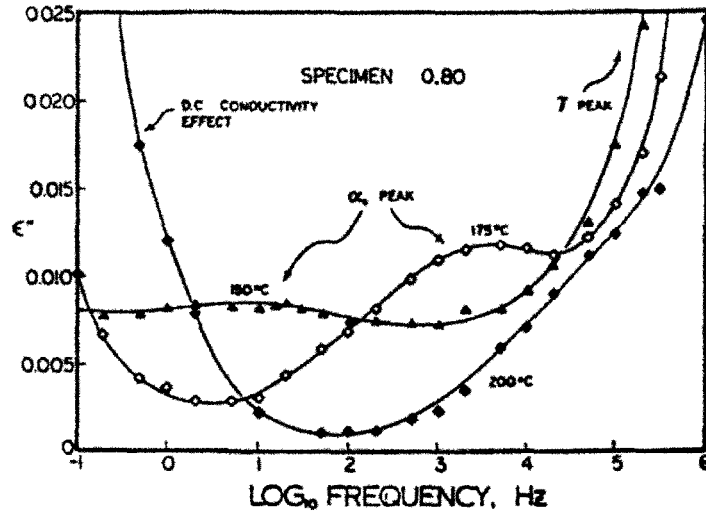


Fig. 5.21 α -relaxation in 80% crystalline PCTFE, (Hoffmann et. al. 1966). (with permission of J. Poly. Sci.)

Equations (5.13) and (5.14) are equally applicable to polymers at the glass transition temperature. William, Landel and Ferry³⁵ have assigned approximate values $W_{\eta} = 0.18$ eV, $T_c \cong T_G - 51.6$ to cover many amorphous polymers. The essential idea is that the activation energy for the β -relaxation is temperature dependent according to, after substituting the WLF constants,

$$\varepsilon_{\beta} = \frac{0.18 T^2}{(51.6 + T - T_g)^2} \quad (5.15)$$

where W_{β} is the energy for the β - process. There is good agreement between the energy calculated using equation (5.15) and that using the ε'' -log f curves. A temperature dependent energy is evidence of the β -process.

Before we proceed further a comment about the application of WLF equation is appropriate. The general equation that applies for the activation energy is:

$$W_{\beta} = \frac{C_1 C_2 T^2}{(C_2 + T - T_0)^2} \quad (5.16)$$

where C_1 and C_2 are called the WLF parameters and T_0 is a reference temperature. The equations (5.15) and (5.16) are valid at $T=T_g$ or $T=T_0$ as appropriate.

D. THE γ -RELAXATION

The method of analysis for γ -relaxation runs parallel to that for β -relaxation though the details are different. The γ -relaxation occurs in both 100% amorphous and semi-crystalline material. Denote the relaxation as γ_a and γ_c in the amorphous and crystalline materials, respectively. The area under the curve of $\epsilon''\text{-}\log f$ curve indicates that γ_a is twice as intense as γ_c . Moreover two other major differences are discernible. They are (a) γ_a is broader than γ_c and (b) γ_a is symmetrical and γ_c is asymmetrical about the peak. Hoffman, et. al. suggest that chain ends induce rows of vacancy in the crystal and the molecular chains reorient themselves in the vacancy so induced.

Evidence for a δ -relaxation is also obtained in the frequency range of $10^8 - 10^{10}$ Hz. though it was not observed in the temperature variable mode because the sample temperature could not be lowered without obtaining a change of phase.

We have followed the analysis of Hoffman et. al. in considerable detail for the purpose of elucidating the line of reasoning that is necessary to interpret the experimental measurements. The material should be viewed as an aggregate of its electrical, optical, mechanical and thermal properties for extracting a consistent picture of the relation between structure and properties. A piece-meal evaluation based on a narrow segment of data should always be treated with caution.

5.4.4 POLYCARBONATE

Polycarbonate is transparent and is as strong as steel. The aromatic rings in the back-bone give it a high melting point of $\sim 265^\circ\text{C}$.

The dielectric properties of polycarbonate is interesting from several points of view³⁶. The polymer has high impact strength below the glass transition temperature and it has been suggested that the large free volume trapped between segments in the amorphous state may account for this behavior. Alternately the high impact strength has been linked, in an empirical way, to the low temperature β -loss.

In most polymers this relaxation has been attributed to the motion of side groups which can occur at temperatures well below T_G . If both relaxations occur in the same main chain then the relationship between the two transitions can be obtained with reasonable certainty. This is thought to occur in polycarbonate in the group $-\text{O}-\text{CO}-\text{O}-$ along the main chain. Polycarbonate is also interesting from the point of view of studying the relationship between the degree of crystallinity and dielectric loss, since this polymer can be prepared in both amorphous and semi-crystalline forms, similar to PCTFE.

The dielectric constant of polycarbonate in the proximity of β -relaxation is shown in fig. 5-22³⁷. The loss factor as a function of frequency is shown in fig. (5.23)³⁸ for the amorphous polymer which has $T_G = 145^\circ\text{C}$. The shapes of the $\epsilon''\text{-log } f$ curves are essentially unaltered which is typical of amorphous polymers for α -relaxation³⁹. The relaxation time decreases with increasing temperature, but the distribution about a mean remains unaltered. The loss curves have sharp maximum and the activation energy calculated from $f_{\max}\text{-}1/T$ plots gives an energy of ~ 6.50 eV.

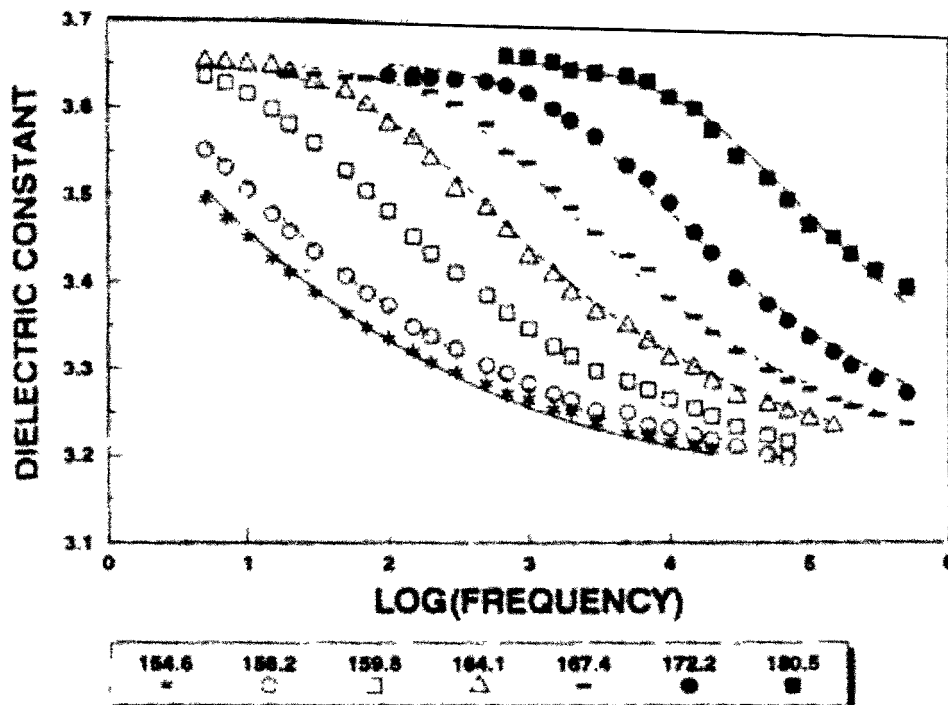


Fig. 5.22 Dielectric constant of polycarbonate in the β -relaxation region. Temperature range as shown (Havriliak and Havriliak, 1997, with permission of A. Chem. Soc.)

We have already seen that such high energy is characteristic of β -transition of amorphous polymers. The shift in the peak with temperature can be used to calculate the specific volume using theory developed by William, Landel and Ferry. The amorphous polymer is shown to have large specific volume compared with the dimensions of a unit cell in the crystalline structure. Matsuoka and Ishida calculate the occupied volume of the T_G state which shows that it is lower than the specific volume. These data show that amorphous polycarbonate has enough free space to allow molecular motion.

The shape of the α -relaxation of the amorphous polymer, while independent of temperature, is dependent upon the degree of crystallinity. The width of the peak of the α -relaxation increases as the crystallinity is introduced. The maximum value does not

appear to be affected. Such behavior has also been observed in other polymers, for example in polyethylene terephthalate [PET]⁴⁰. Increasing the crystallinity makes the peak broader. It is argued that the introduction of crystallinity imposes tension on the amorphous polymer chains and such tension results in a broader ϵ'' - $\log f$ curve.

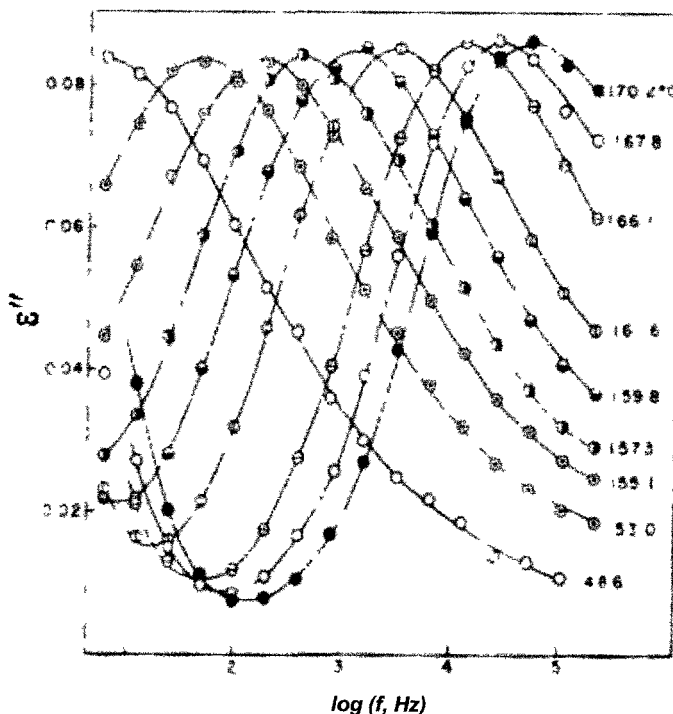


Fig. 5.23 Loss factor of amorphous polycarbonate near the primary relaxation region. (S. Matsuoka and Y. Ishida, 1966, with permission of J. Poly. Sci.).

The low temperature (~ 150 K) relaxation shows characteristics which are counter to the α -relaxation, namely, they are not sensitive to the degree of crystallinity but change with temperature. With increasing temperature above 161 K the loss curves become less broad as shown in fig. (5.24). Increasing width means that there is resistance to motion and this resistance probably comes from the chains in the local regions surrounding the moving part. In the terminology of relaxation studies a broad distribution means a distribution of relaxation times and the mean relaxation time is higher.

Table 5.6 summarizes the glass transition and β -relaxation temperature for several polymers obtained from both electrical studies. An empirical relation that the ratio T_β / T_G has a value of 0.5 - 0.75 has been suggested by Matsuoka and Ishida and polycarbonate has a much lower value of 0.36, meaning that the γ -transition occurs at an unusually low temperature. The temperature difference ($T_\beta - T_\gamma$) for amorphous polycarbonate is much higher than that for Polyethylene terephthalate (PET). This fact is interpreted as favorable to transfer mechanical energy, by allowing motion down to very low temperatures resulting in the high impact strength of this polymer.

A more recent study of polycarbonate is due to Pratt and Smith⁴¹ who observed an activation energy of 0.28-0.56 eV for γ -relaxation and 4.97-8.65 eV β -relaxation for polycarbonate. Both relaxations are observed to follow Arrhenius law (5.8).

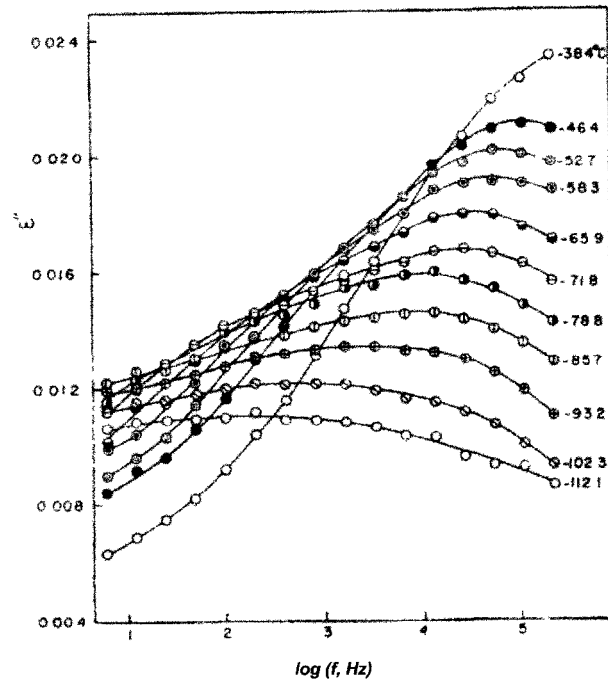


Fig. 5.24 The loss factor in amorphous polycarbonate near secondary relaxation region. The curves become broader as the temperature is lowered. This is attributed to the local motions of the segments of main chain and these motions persist even at lower temperatures (Matsuoka and Ishida (1966). (with permission of J. Poly. Sci.)

Table 5.6

Glass transition and β -relaxation temperature (Runt and Fitzgerald, 1997).

Polymer	T_G ($^{\circ}\text{C}$)	T_{β} ($^{\circ}\text{C}$)	ω_p (Hz)	T_{β} / T_G	Ref.
Electrical					
Poly(vinyl chloride)	100	0	100	0.73	42
Polychloroprene	-30	-85	100	0.77	43
Poly(vinyl acetate)	30	-80	100	0.57	44
Poly(vinyl benzoate)	100	-70	100	0.55	42
PMMA, atactic	120	40	100	0.80	45
Poly(ethylene terephthalate)	90	-50	100	0.61	46
Poly(ethylene adipate)	-40	-120	100	0.66	44
Polycarbonate	150	-120	100	0.36	37

5.4.5 POLY(METHYL METHACRYLATE)

Poly(methyl methacrylate), abbreviated as PMMA, is a transparent polymer with tough outdoor characteristics. Its optical clarity and easy machinability combined with high mechanical strength makes it an excellent substitute for glass. It has bulky side group giving it an amorphous structure. Such polymers are generally known as glassy polymers, not to be confused as polymers not possessing a glass transition temperature. It is completely recyclable. When heated at 300°C it yields almost entirely the original quantity of the monomer, the depolymerization taking place due to a weak chain breaking under the influence of heat. It is resistant to many chemicals but has many solvents such as acetone. The commercial form is atactic, though isotactic and syndiotactic forms which are crystallible have been prepared. The refractive index measured at room temperature is $n = 1.47$.

The dielectric properties of PMMA has been studied by Bergman et. al.⁴⁷ in its *s*-form, and by Ishida and Yamafuji⁴⁸ in its *α*-form. The latter study is referred to here to provide a necessary background, and the more recent literature will be described subsequently.

There is some confusion in the literature with regard to designation of peaks in PMMA and other acrylates. According to Hoffmann et. al (1966) amorphous polymers do not exhibit α -peak and only the peak above T_G should be designated as β -relaxation. The next lower temperature peak should be designated as γ -peak. Bur (1984) also adopts this nomenclature. To avoid confusion we follow the nomenclature used by several authors which is due to Ishida and Yamafuji.

Fig. (5.25) shows the dielectric constant and loss factor in atactic PMMA with $T_G = 105^\circ\text{C}$ over a wide range of frequencies and temperatures (Ishida & Yamafuji, 1961). At 35°C there is a single relaxation at about 150 Hz. This is β -relaxation. Broadhurst and Bur (1984) have observed two relaxations, one at 30 Hz which is identified with this relaxation, and a second smaller δ -relaxation at 1 MHz due to absorbed moisture. As the temperature increases towards T_G the relaxation frequency shifts to higher values and ϵ''_{max} also becomes larger.

The higher temperature, low frequency (~ 30 Hz) relaxation in fig. (5.25) is the α -relaxation. This relaxation is difficult to see at the onset temperature of 137°C because the ionic conductivity is very dominant. However a close examination of the $\epsilon' - \log f$ curve shows that the dielectric constant at this temperature decreases in two distinct steps. The first decrease is due to the α -relaxation and the second due to the β -

relaxation. A plot of $\log f_m$ versus $1/T$ for the β -peaks yields an activation energy of ~ 0.8 eV.

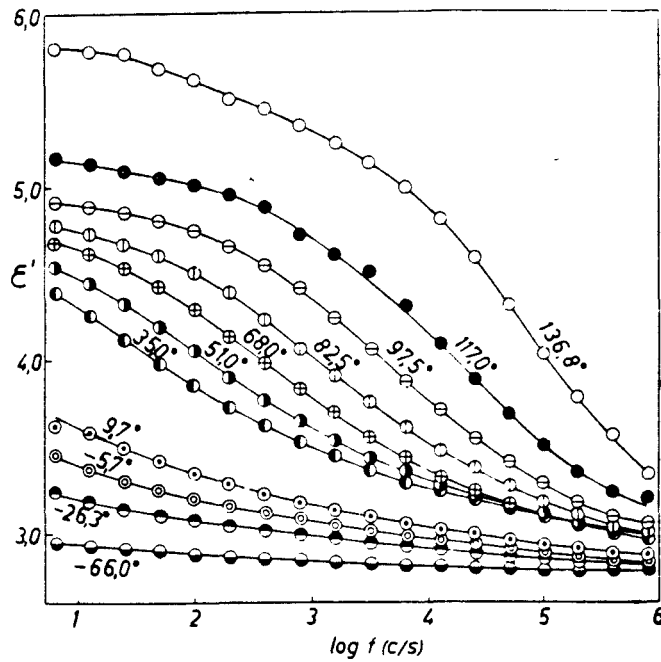


Fig. 5.25 (a). Dielectric constant of atactic PMMA (Ishida & Yamafuji, 1961, with permission of Dr. Dietrich Steinkopff verlag, Darmstadt, Germany).

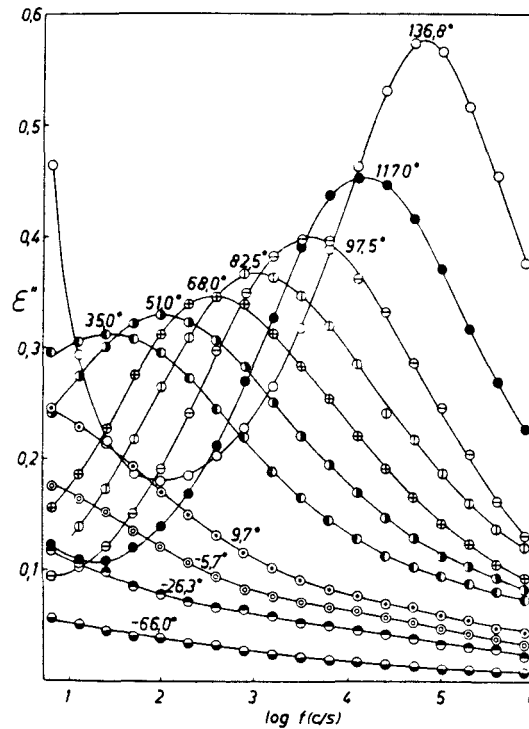


Fig. 5.25 (b). Loss factor in atactic PMMA (Ishida & Yamafuji, 1961). (with permission of Dr. Dietrich Steinkopff verlag, Darmstadt, Germany).

PMMA has two kinds of dipoles; the ester group (O=C-O) and the methyl group (CH₃). While the methyl group with a dipole moment of 0.4 D is short and fixed to the main chain rigidly, the ester groups are long and loosely attached to the main chain. The main dipole in PMMA is the O=C-OCH₃ group in the side chain of PMMA molecule, and it has a dipole moment of ~1.8 D. In this respect PMMA differs from PVC which has the dipole in the main chain and relaxes in the mode of crank shaft motion. At temperatures much lower than T_G the motion of the main chain is frozen and the ester group is active with micro-Brownian motion resulting in γ -peaks. The γ -relaxation is more dominant than the β -relaxation because the latter involves the main chain.

We shall now consider the *s*-PMMA which has the glass transition temperature at 131°C. The merging of the two relaxations occurs at some temperature above T_G . As the temperature is lowered towards T_G the β -relaxation slows down and merges with the α -relaxation that occurs below T_G . The merging of the two relaxations is important to understand the transitions that occur at T_G .

Bergman, et. al (1998) have used measurement frequency in the range of 10^{-2} Hz-1000 MHz over a temperature range of 220 K-500 K. They devote attention to the merging of α - and β -relaxation in the vicinity of T_G , though the latter is pronounced as discussed above. Fig. 5.26 shows the loss factor of syndiotactic PMMA. The loss curves show the familiar peaks and as the temperature is increased f_{max} becomes higher. Moreover the peaks become more narrow as the temperature is increased. At high temperature, $T \sim 400$ K, conductivity contributes to ϵ'' at lower frequencies, < 1 Hz. As the inset of Fig. 5.26 shows the merging of α - and β -relaxation is initiated at 410 K ($T_G = 404$ K). At 370 K, which is below T_G , only the β -relaxation occurs. 420 K is close to, but slightly higher than T_G , and the merging of the two relaxations dominates the loss characteristics. 470K is well beyond T_G and presumably the contribution due to β -relaxation is negligible, if not totally absent.

The relaxation parameters can also be found by using the so called KWW equation (Kohlrausch William-Watts) and transforming data from the time domain to the frequency domain. The frequency domain data may also be transformed to the time domain using Laplace transforms and evaluating the distribution of relaxation times. This aspect of the analysis is deferred till ch. 6. The curves are fitted to the Havriliak-Negami function (eq. 3.72)

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = [1 + (j\omega\tau_0)^{1-\alpha}]^{-\beta} \quad (3.65)$$

where τ_0 is the mean relaxation time and, α and β are empirical constants applicable to the material.

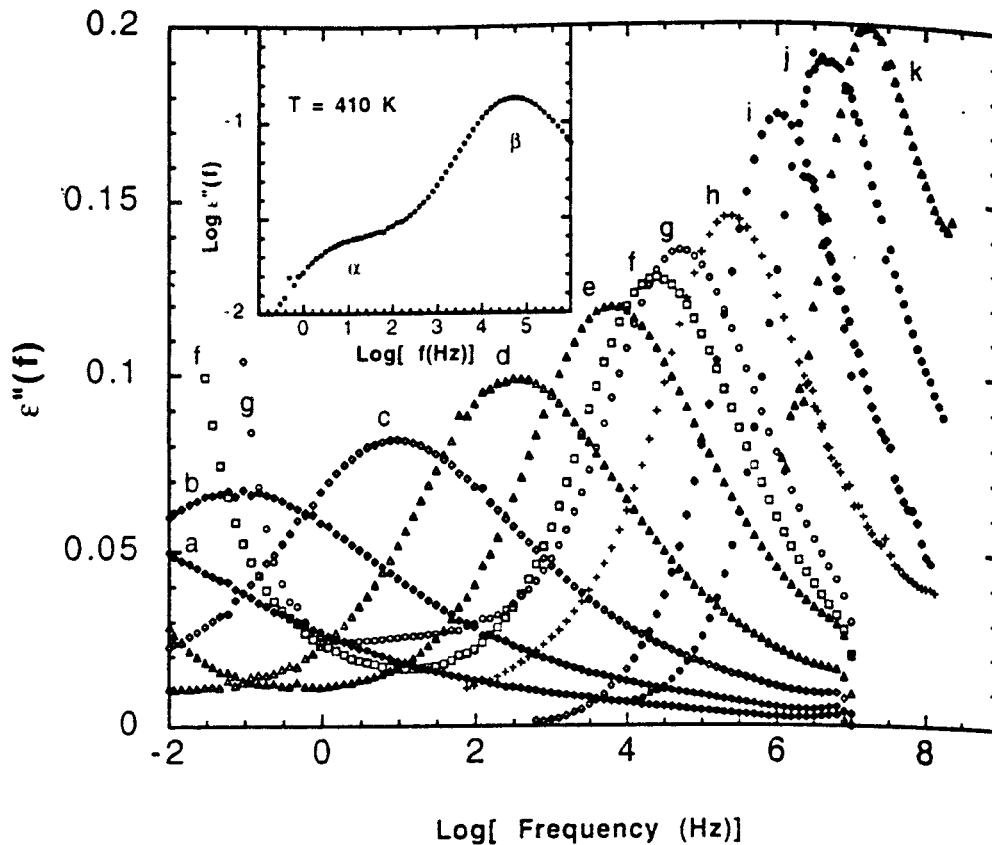


Fig. 5.26 Loss factor in s-PMMA as a function of frequency at various temperatures. Curves (a-e) correspond to temperatures below T_g : 220, 260, 300, 340, and 340 K. Curve (f) to 400K (close to T_g). (g) to (k) to temperatures above T_g : 410, 430, 450, 470 and 490 K. Curves (f) and (g) also show the contribution from conductivity at low frequencies. Curve g ($T=410\text{K}$) is also shown in the inset in a log-log representation with the conductivity subtracted, in order to facilitate recognition of the α -process (Bergman et. al. 1998, with permission of J. Chem. Phys.)

A word of caution is appropriate here to avoid confusion over the choice of symbols for α -relaxation of the polymer and α -parameter for the dispersion. The two alphas are entirely unrelated. α -relaxation is a property that depends on the order-disorder in the polymer whereas α -parameter is a proposed empirical constant. To avoid confusion we always associate α - with its noun such as α -parameter or α -relaxation. Further the α -parameter will be underlined in this chapter only to emphasize that it has meaning only with reference to the dielectric data in the complex plane. Similar comments apply to β -relaxation.

The loss curves at 370 K (well below T_g) and 470 K (well above T_g) show good fit with the Havriliak-Negami function as shown by the full curves, but in the merging

region the fit is poor. However by choosing two such functions, each having its own parameters, and adding the superposition principle, results in good agreement. The β -parameter is approximately constant from 280 K-450K and the α -parameter increases linearly. This is equivalent to the qualitative observation that the α -relaxation gets narrower as the temperature increases beyond T_G and the β -relaxation retains the shape as the temperature is lowered below T_G .

Fig. (5.27) shows the relaxation time τ evaluated using several methods of analyses referred to above. These are: (1) H-N function fit (2) KWW transformation (3) Williams' method of transformation, (see Ch. 6). However above this temperature there is some deviation which is attributed to the merger phenomenon.

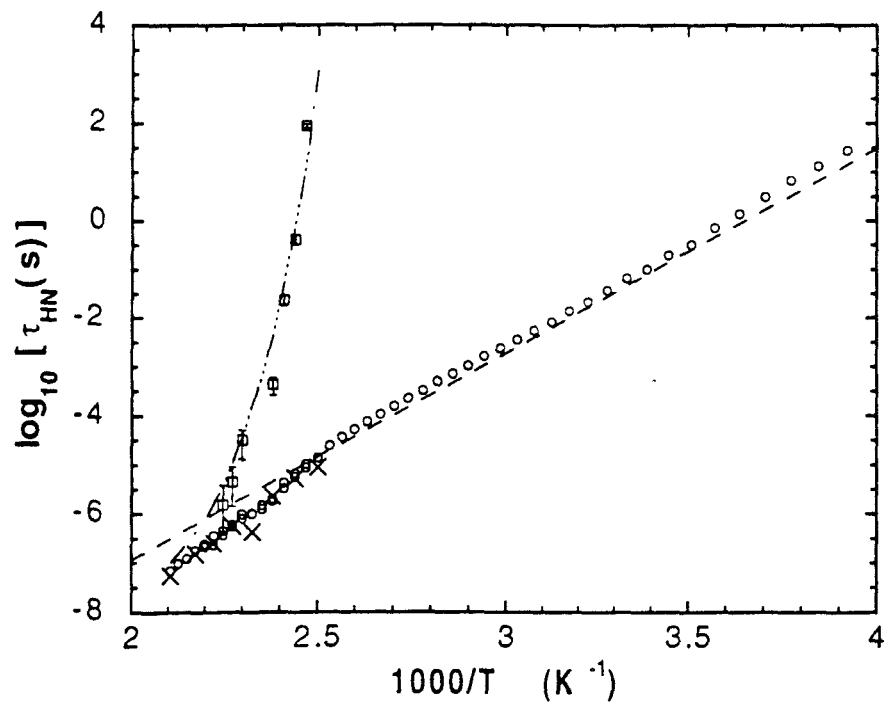


Fig. 5.27 Relaxation times obtained from fitting $\epsilon''(f)$ to a sum of two HN equations. The open square symbolizes τ_a and open circles the effective τ_b as obtained by H-N fits. The x-symbols stand for the τ_b obtained from KWW fits (ch. 6). The dashed and the dash-dotted lines represent the Arrhenius and VF behavior of the β - and α -relaxations respectively (Bergman et. al. 1998). (with permission of J. Chem. Phys.)

The magnitude of the β -relaxation process, below $T < T_G$, increases with temperature according to

$$\epsilon_s - \epsilon_\infty = 0.373 + 7.17 \times 10^{-3} T; \quad T < T_G \tag{5.17}$$

Many polymers show this increase for β -relaxation that may be attributed to increased number of dipoles relaxing or the amplitude of motion increasing because of an increase in free volume. The linear dependence is terminated at T_G . The relaxation time for the α -relaxation τ_α is also temperature dependent; τ_α decreases with increasing temperature changing very sharply at T_G . This kind of behavior makes the polymer very fragile. The relaxation time follows the Vogel-Fulcher equation:

$$\tau_\alpha = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right) \quad (5.18)$$

Where D is a constant and T_0 is the temperature at which the plot of the $1/T - \ln \tau$ line departs from linearity. T_0 is usually 50K lower than T_G in many polymers. The values for α -relaxation may be approximated to: $\tau_0 = 14.8$ ps, $T_0 = 371$ K and $C = 2.27$. Note the very high α -relaxation time of 100s at a temperature of ~ 415 K.

Selected activation energies for the α - and β - relaxations in PMMA are shown in Table 5.7⁴⁹. The relaxation mechanism in *s*-PMMA may be summarized as follows:

1. Both α - and β - relaxation are asymmetric, though the latter is the dominant process.
2. There is evidence for the fact that the two processes are statistically independent and there is no need to invoke any change of relaxation mechanism.
3. In thin samples of isotactic PMMA (10 nm thick) the β -relaxation (local) is observed to be independent of thickness whereas the α -relaxation (dynamic glass transition) is thickness dependent. With decreasing thickness the dielectric decrement ($\epsilon' - \epsilon_\infty$) decreases. (Ref: Dielectric News letter, F. Kramer and L. Hartmann, Sept. 2001).

5.4.6 POLY(VINYL ACETATE)

Poly(vinyl acetate), abbreviated as PVAc not to be confused with poly(vinyl acetal), is a polar polymer; the monomer has ~ 2 D dipole moment and is soluble in aromatic solvents, alcohols and esters. It falls into a category known as poly(vinyl esters). It is amorphous with glass transition temperature of $\sim 31^\circ\text{C}$. Though its dielectric applications are limited it is interesting from two points of view. First, its low glass transition temperature makes it more convenient for study in the region of glass transition temperature. Second it has been quite extensively studied in the time domain and comparing the measured and calculated results often checks the suitability of the applied transformation techniques to the frequency domain. Poly(vinyl acetate) exhibits both α - and β -relaxations. The more recent measurement of the complex dielectric constant of

PVAc is due to Mashimo, et. al.⁵⁰, Nozaki and Mashimo⁵¹ and Dionisio, et.al.⁵² in the frequency domain.

Table 5.7

Selected values of activation energies for α - and β -relaxations in PMMA.

α -relaxation (eV)	β -relaxation (eV)	Reference
	0.92	Mead and Fuoss (1942) ⁵³
	0.91	Bröns and Müller (1950) ⁵⁴
	0.79, 0.87	Deutsch, et. al., (1954) ⁵⁵
4.35		Heijboer (1956) ⁵⁶
3.16	0.61	de Brouckere & Offergeld (1958) ⁵⁷
	0.91	Mikhailov (1958) ⁵⁸
	0.83	(Ishida and Yamafuji) ⁴⁸
	0.79	Reddish (1962) ⁵⁹
5.25		Lewis (1963) ⁶⁰
	0.74, 0.76	McCrum and Morris (1964) ⁶¹
3.47 to 4.30	0.83 to 0.99	McCrum et. al. (1967) ⁶²
	0.78	Thompson (1968) ⁶³
10.62	0.91	Sasabe and Saito (1968) ⁶⁴
	0.93	Kawamura, et. al. (1969) ⁶⁵
	1.15	Solunov and Ponevsky (1977) ⁶⁶
4.35	0.86	Hedvig (1977) ⁶⁷
4.35 $\pm$ 1.04	0.87 $\pm$ 0.06	Gilbert, et. al. (1977) ⁶⁸
	0.74 – 1.09	Vanderschuren and Linkens (1977) ⁶⁹
	0.83	Mashimo et. al. (1978) ⁷⁰
7.25 $\pm$ 1.04	0.97 $\pm$ 0.07	Pratt and Smith (1986) ⁴⁹

(with permission of Polymer)

A. β -RELAXATION

The low temperature ($T < T_G$) loss factors, due to Ishida et. al. (1962), are shown in figs. 5.28 covering a temperature range of -61°C to -6.8°C and a frequency range of 100-1MHz. PVAc clearly exhibits the relaxation process at each temperature and as the temperature is increased f_{max} shifts to higher values. The low temperature relaxations are due to β -relaxation which is attributed to the micro-Brownian motions of the side groups accompanied with the local distortions of the main chains. The low temperature β -relaxation curves are symmetrical about f_{max} as shown in fig. 5-28. Broadening of the β -relaxation occurs as the temperature is increased towards the glass transition, probably due to the overlap of the two relaxations. At sufficiently low temperatures only, we get

the pure β -relaxation and from an analysis the dipole moment of the side group is obtained as 1.7 D and the number of side groups as $4.9 \times 10^{27} \text{ m}^{-3}$. The activation energy for the α - and β -relaxations are 2.6 eV and 0.43 eV respectively. At $T \ll T_G$, $(\epsilon_s - \epsilon_\infty) = 0.35$. We shall refer to these values again in Ch. 6.

B. α -RELAXATION

Fig. 5.29 shows the loss factor data for temperatures in the region of the glass transition ($\sim 30^\circ\text{C}$). Again a relaxation peak is observed at each temperature. A plot of the normalized ϵ'' ($\epsilon''/\epsilon_{\max}$) versus the normalized $\log f$ ($f/f_{\max}$) shows that they lie on a single curve and therefore there is no change in the shapes of loss factor curves with temperature. The high temperature plots exhibit Cole-Cole arc in the complex plane plots of ϵ^* as shown though H-N function is more appropriate as has been discovered recently. The α -relaxation is attributed to the re-orientations of the dipoles due to the segmental motions of the main chains.

The β -parameter together with other parameters are shown in Table 5.8. The constant value of the β -parameter shows that the shape of the loss factor curve remains nearly the same with change in temperature. We recall that $\beta = 1$ yields Debye relaxation. The dielectric decrement decreases with increasing temperature as shown in fig. 5.29 and Table 5.8 This does not imply that the dipole, in the relaxed state, has a lower dipole moment. The dipole moment calculated at the measured temperatures (see chapter 2 for the method) shows that the dipole moment is ~ 2 D at all temperatures, higher than that of the monomer, 1.6 D.

The data of Dionisio et. al (1993) shows that WLF equation is satisfied for the activation energy in the temperature range of α -relaxation. The activation energy obtained from the plot is 2.35 eV which is in the expected range. The results in PVAc may be concluded as follows:

1. There are two relaxations, the main relaxation occurring at $\sim 29^\circ\text{C}$. The main relaxation is much stronger and it is attributed to the re-orientations of the dipoles due to the segmental motions of the main chains.
2. Almost all of the mean square dipole moment $\langle \mu^2 \rangle$ is carried into the α -relaxation.
3. The β -relaxation occurs at -61°C at 1 kHz.

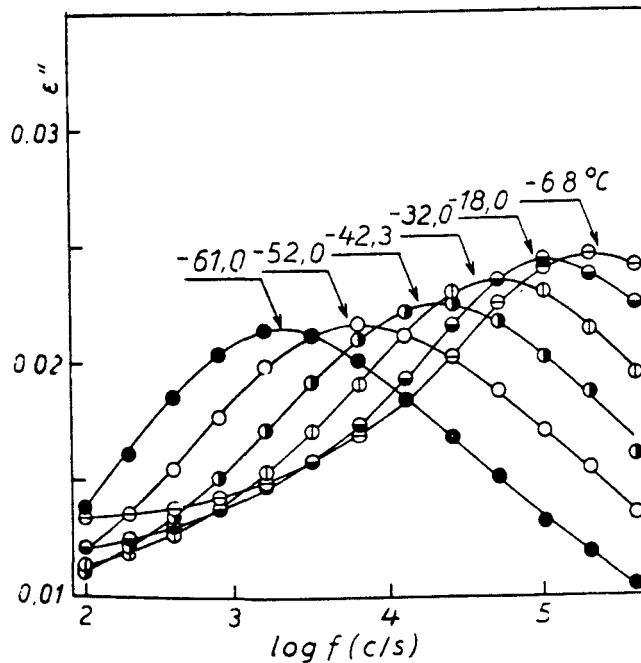


Fig. 5.28 Dielectric loss factor in PVAc at low temperatures showing β -relaxation. The curves become broader as the temperature is increased due to the over-lapping α -relaxation (Ishida et. al, 1962, with permission of Dr. Dietrich Steinkopff Verlag, Darmstadt, Germany).

Table 5.8

α -relaxation parameters in Poly(vinyl acetate), (Dionisio, et. al., 1993).

$T(^{\circ}\text{C})$	$f_{\max}(\text{kHz})$	$\tau_0(\text{s})$	$\epsilon''_{\max} C_0^a$ (pF)	$(\epsilon_s - \epsilon_{\infty}) C_0$ (pF)	β - parameter
45	0.0343	4.64×10^{-3}	14.90	54.9	0.56
50	0.1658	9.60×10^{-4}	14.69	50.2	0.58
55	0.6036	2.64×10^{-4}	14.33	47.9	0.59
60	2.0484	7.77×10^{-5}	13.87	46.2	0.60
65	5.8080	2.74×10^{-5}	13.68	45.0	0.61
70	15.8742	1.00×10^{-5}	13.39	43.0	0.61

(a) C_0 is the capacitance of the measuring cell, 7.9 pF

5.4.7 POLYSTYRENE

Polystyrene, abbreviated as PS, consists of linear chain and is chemically inert. It has many organic solvents. It cannot be used above 85°C due to heat distortion and is unsuited for outdoor applications. The glass transition temperature is $\sim 100^{\circ}\text{C}$ and melting point is 250°C . The molecular mass is between 200,000-300,000. Addition of

plasticizers lowers T_G depending upon the quantity and the type of compound used. For example T_G of PS can be lowered to as low as -150°C by adding just 1% of methyl acetate.

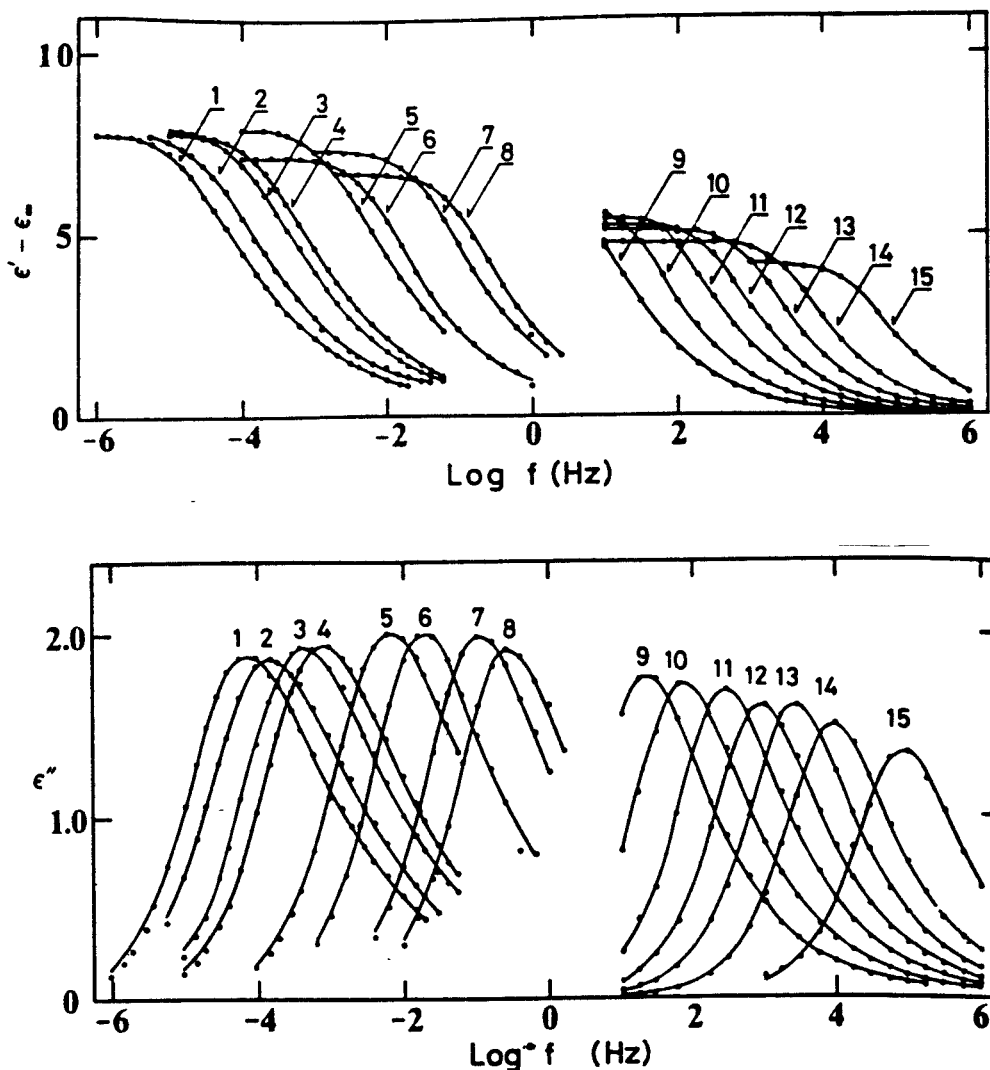


Fig. 5.29 Dielectric constant and loss factor in PVAc in the region of T_G . Temperatures are: 1-301.25K, 2-301.71K, 3-302.90K, 4-303.60K, 5-305.80K, 6-309.16K, 7-311.15K, 8-315.65K, 9-326.25K, 10-330.47K, 11-335.05K, 12-339.30K, 13-343.75K, 14-349.80K, 15-365.95K. Solid curves will be referred to in ch. 6. (Mashimo, et. al., 1982, with permission of J. Chem. Phys.)

Plasticizers are usually low molecular weight non-volatile compounds that increase the flexibility and processibility of polymers. The plasticizing molecules, being much smaller than a polymer chain, are capable of penetrating the chain like bugs in woodwork. They establish attractive polar forces with chain segments there by reducing the cohesive forces between chains. This increases chain mobility and correspondingly, lowers T_G . The commercial PS is atactic and therefore amorphous though an isotactic

form with about 30% crystallinity can be prepared. PS has low water absorption, ~0.03% though moisture attacks it more vigorously than polyethylene. It has a small dipole moment of 0.26D due to the asymmetry at the phenyl side group (C₆H₅).

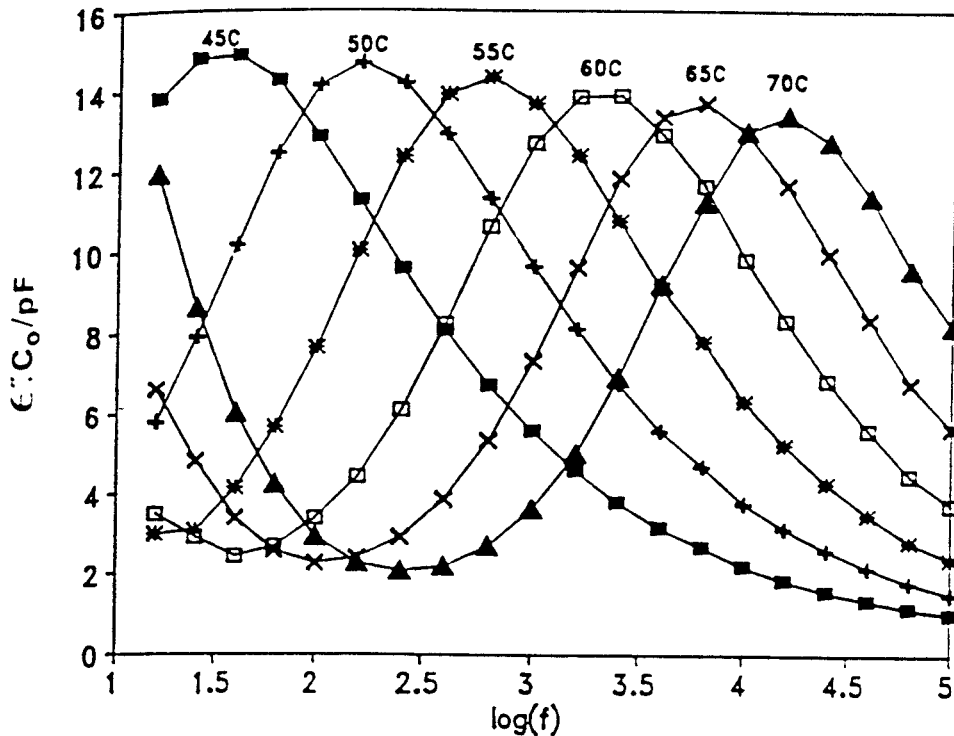


Fig. 5.30 The dielectric loss factor in PVAc above T_g showing α -relaxation. With increasing temperature the peak is marginally reduced. The area under the peak shows the number of relaxing dipoles and the decrease in height, without change in shape, indicates a decrease in the total amount of relaxed dipoles with increasing temperature (Dionisio et. al., 1993, with permission of Polymer).

In certain applications such as encapsulation and cable termination, the procedure involves *in-situ* polymerization. Unmodified PS can be made into films and used in capacitors and radio frequency cables because of low loss. Its high insulation resistance and ability to retain charge for a long period is also an advantage in capacitor applications. Glass reinforced PS has been successfully used as base for printed circuit boards and for microwave strip line circuits because of a low dielectric constant and high dimensional stability.

We refer to the results of Yano and Wada⁷¹ who studied three forms of PS. The types and some of their physical properties are given in Table 5.9. The measurements were performed on PS films 150 μm -250 μm thick in the frequency range of 30 Hz-100kHz covering a temperature range of 250 K- 400 K.

Table 5.9
Polystyrene samples used by Yano and Wada (1971)

Symbol	Type	Average M	Density Kg/m ³
APS	Atactic	2.4×10^5	1050
MPS	Monodisperse	4.1×10^5	1051
IPS	Isotactic	9.2×10^5	1071

Fig. 5.31 shows the complex dielectric constant of atactic polystyrene. Six relaxations are observed in PS, when several techniques (mechanical, NMR) are employed. Of these only three α , β , γ' , are observed in dielectric measurements.

The α -relaxation is due to segmental motion and follows the WLF equation for the temperature dependence of relaxation time:

$$\ln \tau = \ln \tau_0 - \frac{C_1(T - T_0)}{C_2 + (T - T_0)} \quad (5.19)$$

where τ is the relaxation time which is a function of temperature, τ_0 is the relaxation time at an arbitrarily chosen reference temperature $T_0 < T_G$, C_1 and C_2 are constants known as the WLF parameters.

Activation energies obtained from the plots of $\log f_m - 1/T$ are, 1.30 eV, 0.39 eV, 0.12 eV, 0.07 eV for β , γ , γ' and δ processes respectively. Not all the six processes were observed by dielectric measurements. The γ relaxation was not observed at all in this study. The γ' relaxation which was observed clearly in APS is attributed to the introduction of polar impurities during bulk polymerization. This peak appears when the sample is heated at 280°C for 30 minutes providing support for this reasoning. Table 5.10 summarizes the results in PS.

5.4.8 POLY(ETHYLENE TEREPHTHALATE)

Polyethylene terephthalate, abbreviated as PET, has an aromatic ring in the main chain (Table 5.3) and possesses a higher T_G of $\sim 69^\circ - 75^\circ\text{C}$. It melts around 265°C and is resistant to heat and moisture. It is extensively used in textile fibres due to its resistance for wrinkles. Electrical industry uses PET as high performance capacitor foils and polymer electrets. It is available in unoriented, uniaxially and biaxially oriented form. Its

crystallinity can be controlled in the range of 0-60%. The dielectric properties depend on the degree of crystallinity and the method adopted to achieve crystallinity.

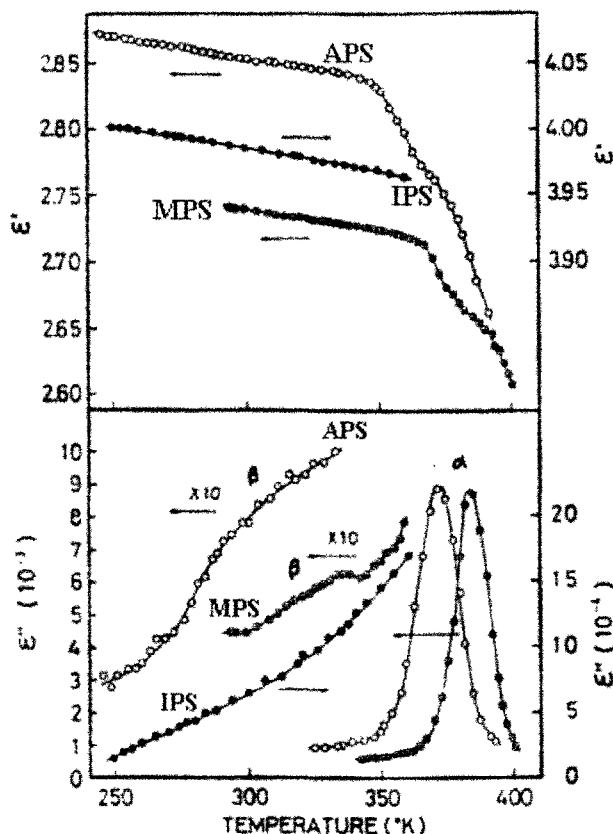


Fig. 5.31 Dielectric constant and loss factor of polystyrene: APS, 110 Hz; MPS, 110 Hz; IPS, 300 Hz (Yano and Wada, 1971, with permission of Polymer).

Table 5.10

Relaxation processes in polystyrene (Yano and Wada, 1971)
(Adapted with permission from J. Poly. Sci.)

Symbol	Temp. (K)	Energy (eV)	Mechanism
α	400	WLF type	Segmental motion of backbone chain
β	350	1.3	Local oscillation of backbone chain
γ	180	0.37	Rotation of phenyl group (not observed electrically)
γ'	97	0.12	Polar defects such as oxygen bonds
δ	55	.07	Defects in tacticity (not observed electrically)
ϵ	(25)	-	Not observed electrically

Being a main chain polymer it possesses both α - and β -relaxations. The α -relaxation is associated with the glass-rubber transition in amorphous regions. The origin of β -relaxation is subject to various interpretations. Recent studies are due to Coburn, et.al.⁷², Miyairi⁷³, Adamec and Calderwood⁷⁴, Tatsumi, et. al.⁷⁵, Dargent, et. al.⁷⁶, Osaki⁷⁷ and Neagu, et. al.⁷⁸.

Fig. 5.32 shows the real part ϵ' and the loss factor ϵ'' above T_G . The α -relaxation is clearly seen, the relaxation frequency shifting to higher values as the temperature is increased from 100° – 150°C. At lower frequencies and higher temperatures the α -relaxation is overlapped with the increase of conductivity as shown in fig. 4.8.

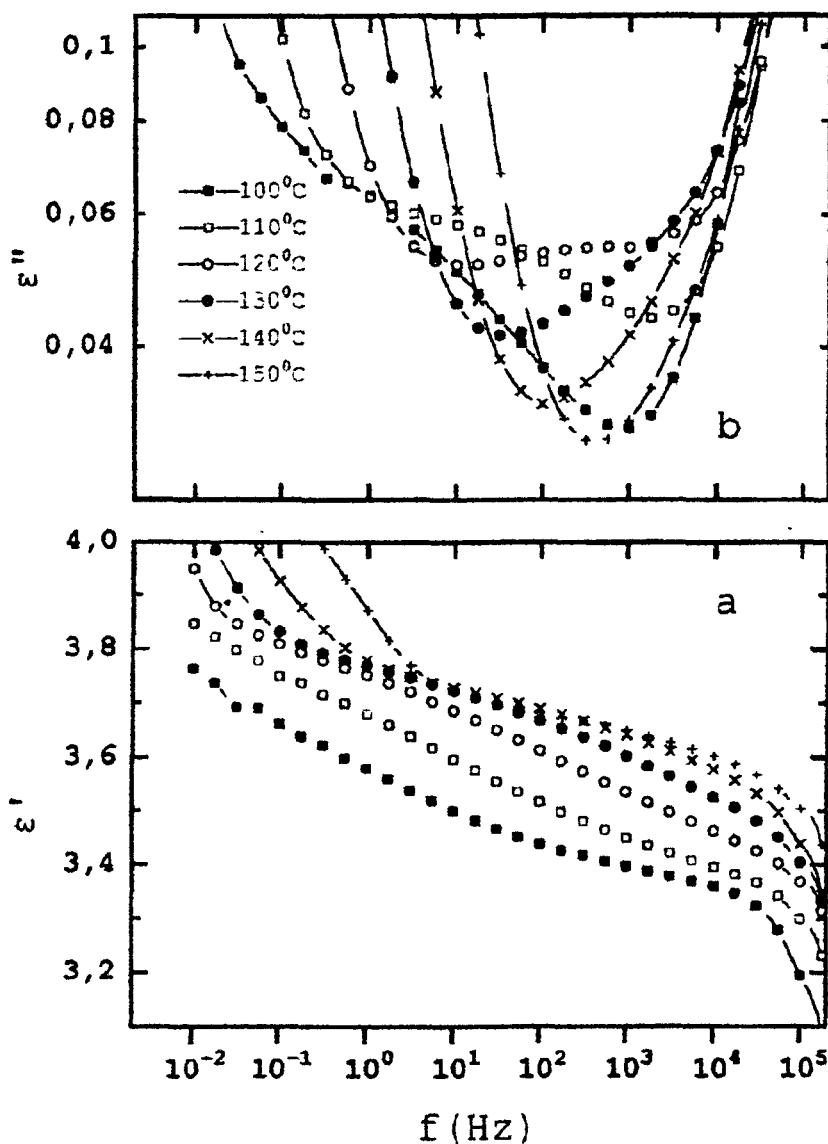


Fig. 5.32 Real part ϵ' and the imaginary part ϵ'' of the dielectric constant of PET exhibiting α -relaxation (Neagu et. al. 1997, with permission of J. Phys. D: Appl. Phys.)

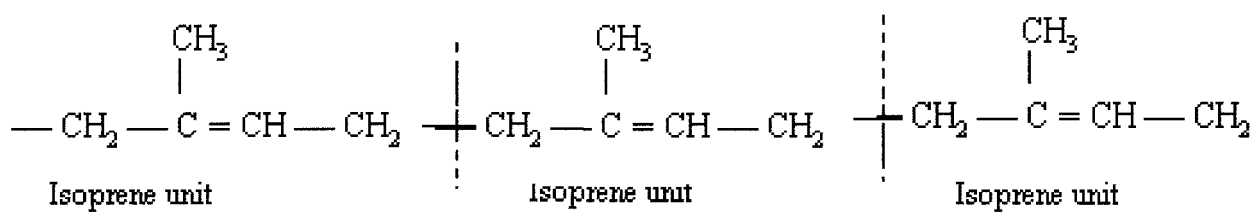
The following conclusions may be drawn with regard to relaxation in PET.

- (1) The α -relaxation is associated with the glass-rubber transition in the amorphous regions. The peak shifts to higher temperatures or lower temperatures with increasing degree of crystallinity. Increasing crystallinity also renders the loss peak weaker and broader possibly due to the constraint it imposes on molecular movement in the amorphous regions.
- (2) The β -relaxation is due to the local movement of the chain. The α -relaxation is much weaker than the β -relaxation.
- (3) At low frequencies and high temperatures both ϵ' and ϵ'' increase due to conductivity effects; the bulk interfacial polarization between the amorphous and crystalline regions possibly causes this increase.

5.4.9 POLYISOPRENE

The degree of crystallinity of a polymer is closely related to the long range order of the molecules, that is, the configuration of the chain. Stereo-regular polymers, isotactic and syndiotactic forms, are crystalline; atactics are amorphous. This is the reason for the high density of linear polymers like HDPE exhibiting crystallinity up to 90% while LDPE, which is branched, has only 40% crystallinity. Branched polymers do not crystallize as easily as linear polymers do. Polyisoprene is another example. It has two possible geometrical arrangement of the molecules. In the first, the molecules of isoprene bend back giving the chain a coiled structure. This type of isomer is called *cis*-1,4 polyisoprene and it is the synthetic version of natural rubber. On the other hand, in the *trans*-isomer, isoprene molecules are packed more straightly, giving it a rod-like structure, and this form is known as *trans*-1, 4 polyisoprene which is the synthetic version of gutta percha. Gutta percha has, therefore, more crystallinity.

Polyisoprene, like polystyrene undergoes depolymerization to yield the monomer to a limited extent. Under pressure scission of monomer connecting bonds ($\text{CH}_2 - \text{CH}_2$) occurs and big molecules are broken into smaller units. The structure of polyisoprene is:



The polymer bears components of the dipole moment both parallel and perpendicular to the chain backbone. Pressure exerts a greater influence on the segmental motion when compared with the longest normal mode. Above T_G global chain motion and local segmental motion occurs and the global chain motion can be activated by lowering the temperature at constant pressure or by increasing pressure at constant temperature. Recent dielectric studies of Floudas et. al.^{79, 80} in polyisoprene are directed towards obtaining the relaxation times under the combined effects of temperature and pressure.

Floudas et. al studied five different samples of *cis*-isoprene with number averaged molecular mass of 1200, 2500, 3500, 10600 and 26000 and identified by these numbers. The glass transition temperatures are 191, 199, 200, 204 and 208K respectively. The samples had a polydispersity of less than 1.1. The molecular mass indicates the degree of entanglement as follows: 20%, 50%, 67%, 200% and 500%. The samples vary from no entanglement to well entangled. The interest of the study lies in understanding the effect of pressure on entanglement as this is of technological interest. Fig. 5.33 shows the loss factor for the PI-1200 under isothermal (top) and isobaric conditions (bottom). Two modes of relaxations are identified as normal (n) and segmental (s). Both modes become slower with increasing pressure and decreasing temperature. The fastest of the modes is due to segmental motion and the spectra of the slower modes are due to normal chain motion. The pressure is changed from 1 bar to 3 bar and the temperature from 205 K to 243 K.

It is easily seen that the temperature is more effective in slowing the normal mode when compared with pressure. The shift in the peak of the normal mode due to temperature change is five decades, whereas the shift due to pressure change is only three decades. Normalized plots of ϵ'' at a reference temperature of 295K or 1 bar shows that the normal mode is independent of temperature or pressure while the segmental mode is dependent on these two factors. The temperature change produces greater deviation than the change in pressure.

The dielectric spectra are analyzed using the Havriliak and Negami function (eq. 3.71) which is generally more successful in the analysis of amorphous polymers near T_G . The rise of the loss curves at $f < 100$ Hz is due to conductivity (eq. 3.8), and the contribution due to conductivity is subtracted from measured ϵ'' .

In all systems the main and secondary relaxations exhibit a temperature dependence according to two laws:

Main relaxation: The Vogel-Fulcher Law.

The V-F law is expressed as

$$\log \tau = \log \tau_0 + \frac{DT_0}{(T - T_0)} \quad (5.20)$$

where $\log \tau_0$ is the limiting value at high T , T_0 the apparent activation temperature of the α -relaxation, sometimes called **Kauzmann temperature** and D the so called fragility parameter. Lower values of D denote increased fragility in the glassy phase.

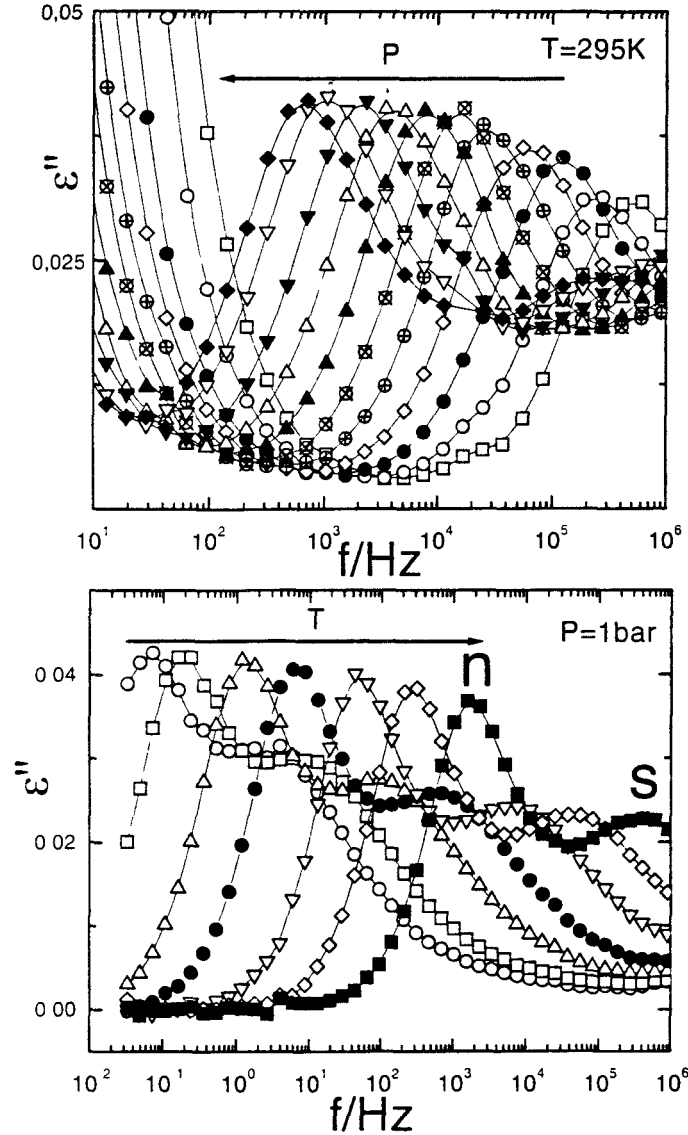


Fig. 5.33 Dielectric loss for PI-1200 plotted under isothermal conditions (top) at 295 K, and under isobaric conditions (bottom) at 1 bar. The corresponding pressures to the isothermal spectra are ($\square$) 1 bar, ($\circ$) 0.3 kbar, ($\bullet$) 0.6 kbar, ($\diamond$) 0.9 kbar, ($\oplus$) 1.2 kbar, ($\otimes$) 1.5 kbar, ($\blacktriangle$) 1.8 kbar, ($\triangle$) 2.1 kbar, (∇) 2.4 kbar, ($\blacklozenge$) 2.7 kbar, ($\blacklozenge$) 3.0 kbar. The temperatures for the isobaric spectra are ($\circ$) 205 K, ($\square$) 208 K, ($\triangle$) 213 K, ($\bullet$) 218 K, (∇) 225 K, ($\diamond$) 233 K, ($\blacksquare$) 243 K. The symbols 's' and 'n' indicate the segmental and normal modes, respectively (with permission of AIP)

Table 5.11

Relaxation parameters in polyisoprene-1200 (Floudas & Gravalides, 1999)

Mode	τ_0 (s)	D	T_0 (K)
segmental	9.2×10^{-7}	4.34	153 ± 1
Normal	1.96×10^{-5}	4.34	149 ± 1

The relaxation time is dependent on both pressure and temperature, though it is for the segmental motion than for the normal chain motion. The relaxation time increases linearly with increasing pressure for both modes. The fact that T_0 for segmental relaxation is higher than that for normal relaxation is interpreted to mean that the $\log \tau - 1/T$ curves cross each other. The combined influence of temperature and pressure has not been investigated as extensively as the influence of temperature alone and has the potential of yielding valuable results in other elastomers.

5.4.10 EPOXY RESINS

Epoxy resins are excellent adhesives having structural strength and they are used in a variety of applications. Araldite is the commercial name of one of the most popular epoxies that can be bought in a hard ware store. They come under the category of **thermo-setting** polymers in contrast with the **thermo-plastic** polymers we have considered so far. Thermo-setting polymers undergo a chemical change when heated and upon cooling do not regain their former characteristics. They are extensively used in electrical industry for potting which is a term used for encapsulation of electrical equipment such as potential transformers and current transformers.

Commercially available epoxies have considerable conductivity and advantage can be taken to study the role of conductivity in relaxation studies. Such studies have been carried out by Corezzi et. al.⁸¹ in three different commercial epoxy compounds, having an increasing number of polar groups. The samples were chosen for the following reasons:

1. The samples attain glassy phase easily avoiding crystalline phase even at the slowest cooling rate.
2. Their dipole moment is due to the same polar group i.e. the epoxy ring, having a moment of 2.1 D
3. They possess appreciable conductivity due to the presence of ionic impurities.

Fig. 5.34 shows the spectra of the loss factor for one sample at various temperatures. Below the glass transition temperature (204K) there is only one small peak lasting over

several decades of the frequency due to the β -relaxation. By increasing the temperature the main α -relaxation is observed and the peak shifts to higher frequencies as the temperature is increased, merging with the β -peak. At lower frequencies ϵ'' increases due to conductivity and the loss factor in this region increases proportional to ω^{-1} (fig. 4.1). In view of the almost perfect linearity observed it is clear that conductivity dominates the dielectric loss in regions where the α -relaxation may be neglected.

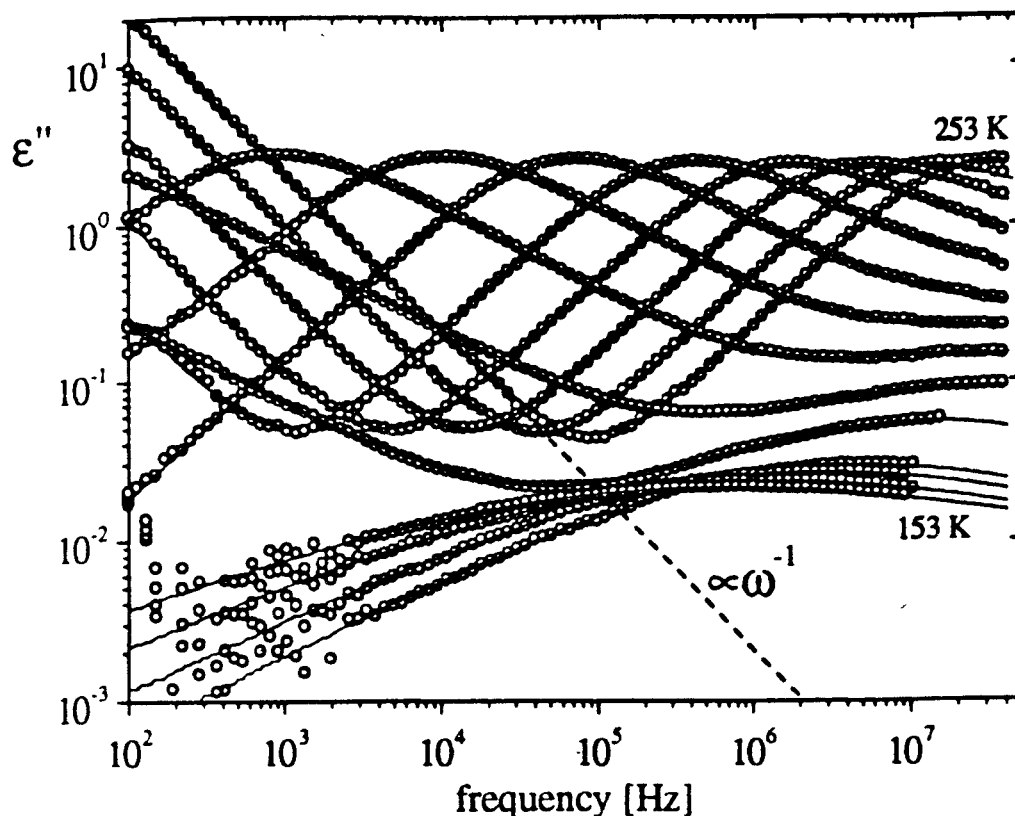


Fig. 5.34 Dielectric loss factor in epoxy resin above and below glass transition temperature. The solid lines represent the fitting equation built up by the superposition of H-N functions and the conductivity term $\epsilon\omega_0$. The dashed line shows the dc conductivity contribution (Corezzi, et. al., 1999, with permission of J. Chem. Phys.)

The loss curves are fitted to Havriliak-Negami function taking into account the conductivity, (eq. 3.109) and the quality of the fit is shown in fig. (5.34) by solid lines. The relaxation time varies in the range of $10^{-10} - 10^2$ s for both relaxations.

5.4.11 POLYAMIDES

Polyamides are either aliphatic or aromatic depending on whether they have CH_2 or benzene in the main chain. Aliphatic polyamides are called **nylons** commercially and

come in a number of different varieties. Nylons are designated according to a numbering system; a single number designates the number of carbon atoms in the monomer, as in nylon 6. Two numbers designate the number of carbon atoms in each of the constituent chemicals (diamine and dicarboxylic acid) as in nylon 6,6 and nylon 6,10. Aliphatic nylons have a melting point in the range of 250°C-300°C. More recently nylons having melting points of 450°C-500°C have become available. Aromatic polyamides are called **aramids** and they have properties that make them suitable for high temperature applications.

More recently polyamide-4,6 with the trade name Stanyl® has become available commercially. The polymer has improved characteristics making it suitable for electrical insulation at elevated temperatures. The improved characteristics arise out of the high number of amide groups per unit chain length when compared with other polyamides. Stanyl® is highly crystalline and has a melting point of 295°C. Its density is 1180 kg/m³ and has a molar mass of $M_w = (4-4.5) \times 10^3$ g/mol.

Fig. 5.35 (Steeman and Maurer, 1992) shows the dielectric constant and the loss factor of dry Stanyl® as a function of temperature at various frequencies. The weak γ -relaxation is due to the rotation of the non-polar CH₂ groups as in other nylons and the β -relaxation is much stronger because the amide bonds are polar. The glass transition temperature is ~90°C and the loss factor curves show the α -relaxation at high frequencies. At very low frequencies, for example at 0.1 Hz this peak is clearly missing, the ϵ'' -T curve rising monotonously. This is due to the interfacial polarization which occurs predominantly at high temperatures and low frequencies. A comparison with fig. 5.2 shows similarities when data are presented in the frequency domain.

The relaxation processes in nylons show three distinct features (fig. 5.35, Steeman and Maurer, 1992).

- (1) A low temperature γ relaxation in the range 125K-175K, probably due to local motion of CH₂ segments in the inter-chain.
- (2) An intermediate β relaxation at ~ 225 K which is related to the rotation of amide bonds (O = C—N—H) together with water molecules that are bonded to them.
- (3) A strong α -relaxation near the glass transition temperature (~325 K).
- (4) Above T_G the polymer becomes highly conductive with the loss factor increasing rapidly. The mechanism is possibly the interfacial polarization (section 4.4) with the charge carriers accumulating at the boundaries between the crystalline and amorphous regions. This kind of relaxation due to space charges is sometimes called δ -relaxation, not to be confused with the low temperature relaxation such as the one observed with polystyrene (Yano and Wada, 1971).

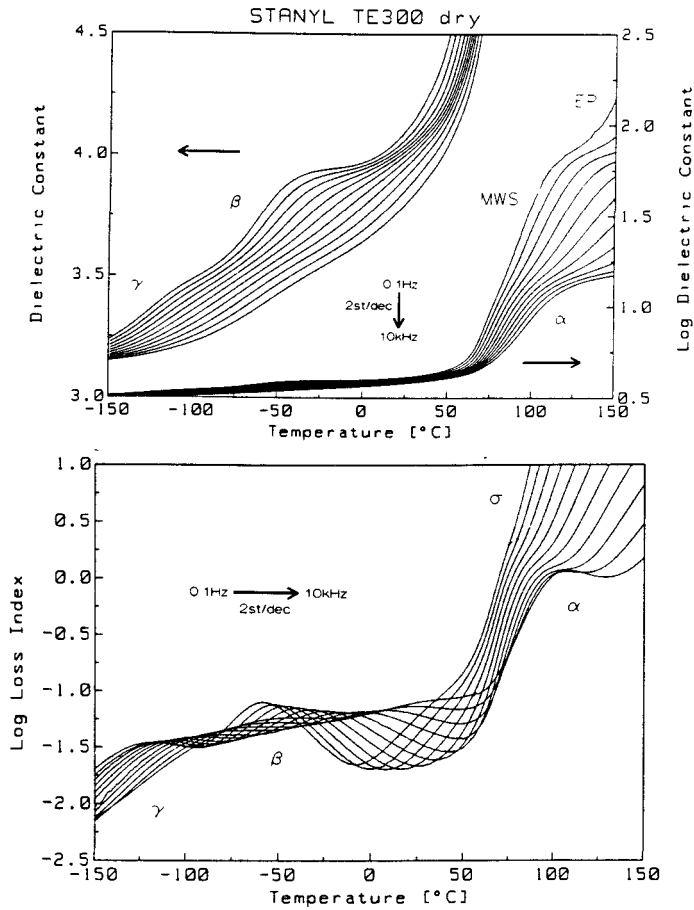


Fig. 5.35 The dielectric constant and loss factor of dry Stanyl® as a function of temperature, for several frequencies. EP stands for electrode polarization which increases the dielectric constant at the highest temperature. MWS stands for Maxwell Wagner Sillars' interfacial polarization which is dominant at higher temperatures and low frequencies (Steeman and Maurer, 1992, with permission of Polymer).

There are two alternative methods to obtain the loss factor due to dipolar processes only. One is to apply equation (3.8) provided σ_{dc} is known. An alternative is to use the approximate equation

$$\epsilon'' \cong -\frac{\pi}{2} \frac{\partial \epsilon'}{\partial \ln(\omega)} \quad (5.21)$$

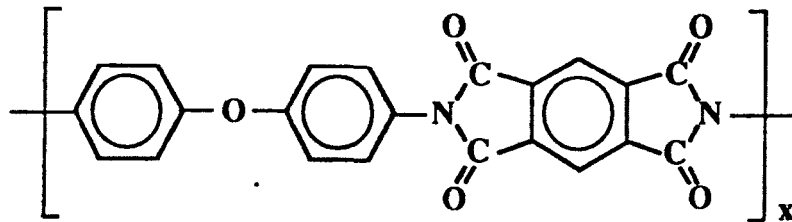
which has the advantage that ϵ' is not influenced by the dc conductivity. Steeman et. al. have used this method and obtained ϵ'' due to dipolar processes only.

The space charge polarization occurs above the glass transition and it is observed only by dielectric measurements. Space charge accumulation usually leads to electrode polarization and an associated increase in the dielectric constant. As expected the

activation energy increases for the relaxation processes in the order γ -, β -, α -process. In engineering applications moisture content is of concern and the effect of moisture is also shown in the relaxation map. With increasing moisture the activation energy appears to decrease indicating that the water molecules assist the relaxation processes. Moisture increases the electrical conductivity which also lowers the temperature at which interfacial polarization shows up.

5.4.12 POLYIMIDES

Polyimide (PI) is a high temperature dielectric with a long chemical name that keeps chemists happy: poly-4,4'-oxydiphenylene-pyromelitimide. However the repeat unit is simpler to understand :



It is commercially known as H-film or Kapton® and is amorphous. It has a glass transition temperature between 260°C - 320°C. Kapton is available in several grades such as corona resistant, antistatic, thermally conductive etc. The polymer has the interesting property that conducting lines can be drawn by irradiation with many pulses of ultraviolet laser radiation, and with many possible practical applications⁸².

Amborski⁸³ has measured the dielectric loss in H-film over the temperature range of -60°C-220°C and Wrasidlo⁸⁴ has extended the higher temperature range to 550°C. Three dielectric loss regions are identified. The dielectric constant and $\tan \delta$ as a function of frequency at various temperatures are shown in fig. 5.43. The width of the loss factor at half peak according to Debye theory is 3.46 (section 3.2) and applies reasonably well to the polymer. The maximum dissipation factor according to Debye theory is

$$\tan \delta_{\max} = \frac{\Delta \epsilon}{\epsilon_{\infty}} \frac{1}{\sqrt{1 + \frac{\Delta \epsilon}{\epsilon_{\infty}}}} \quad (5.22)$$

where $\Delta\epsilon = (\epsilon_s - \epsilon_\infty)$ is the dielectric decrement. It is easy to prove that Equation (5.22) simplifies to (3.37). Substituting $\tan \delta_{\max} = 0.4$ the dielectric decrement is obtained as ~ 6 which agrees with experimental measurements. Since the repeat unit is non-polar except for the diphenyl ether segment which has only 1.15 D, such large dielectric decrement is probably due to amide side group. Since the polymer is amorphous the possibility of glass transition for the peak was considered and found not feasible. The method of calculation is instructive and shown below:

From measurements the aromatic polyimide has the following parameters. $\epsilon_\infty = 2.4$ (fig. 5.36), $\epsilon''_{\max} = 2.0$, molecular weight of repeat unit = 364 gm/mole and density of 1400 kg/m³. Substituting in

$$\epsilon''_{\max} = \frac{\epsilon_s - \epsilon_\infty}{2} \quad (3.34)$$

$\epsilon_s = 6.4$. Onsager's equation (2.77) can be applied at the glass transition temperature. We first calculate the number of repeat units as

$$N = 6.02 \times 10^{23} \times \frac{1400}{342 \times 10^{-3}} = 2.46 \times 10^{27} / m^3$$

Substituting in eq. (2.79) the dipole moment at 573 K is found to be 3.6 D which is much greater than the dipole moment of the repeat unit (~ 1.15 D). Further substitution of $T_g = 573$ K in the WLF equation (5.12a) gives an activation energy of ~ 21 eV which appears to be too high by a factor of ten. Hence the relaxation is not due to the glass transition but occurs in the solid state.

A. INFLUENCE OF MOISTURE

Polyimide films absorb considerable moisture, $\sim 3.3\%$ in an atmosphere of 100% humidity (2500 Pa at 21°C). In fact this property has been utilized in building humidity sensors. The absorbed moisture amounts to two molecules per PI repeat units. The dielectric constant increases upto 20% due to absorption of water. The increase occurs even below room temperature, in the range of 80 K-270 K.

Fig. 5.37⁸⁵ shows the loss factor of 'dry' film and a single peak is observed at each frequency. In the dry film the familiar characteristic of peak shifting to higher temperature as the frequency is increased is seen. Arrhenius plots give an activation energy of 0.53 eV and a relaxation time of 10^{-16} s. This peak could be eliminated by drying the film for at least 250 days; this suggests that the observed relaxation is

possibly due to the presence of the moisture and not due to the intrinsic property of the polymer.

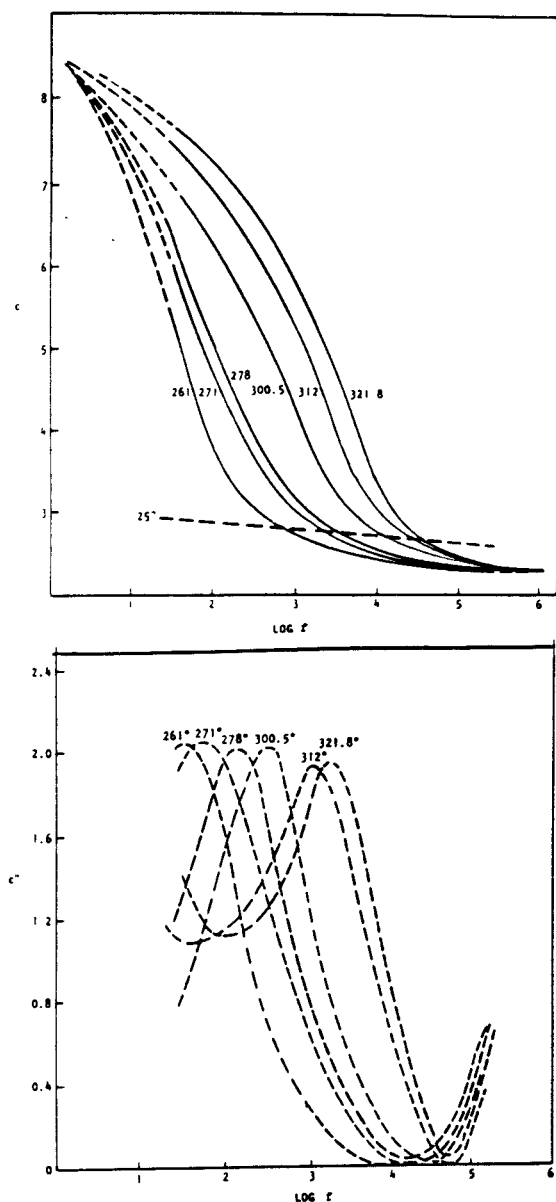


Fig. 5.36 ϵ' and loss tangent versus $\log (f)$ at various temperatures in PI. (1) 261.5°C, (2) 271°C, (3) 278°C, (4) 282°C, (5) 300.5°C, (6) 312°C, (7) 321.8°C (Wrasidlo, 1972). (with permission of J. Poly. Sci.)

In contrast to the dry film, films that have absorbed moisture show two distinct peaks, the sharpness of the peak increasing with the moisture content. The peak exhibited by the dry film also increases in magnitude. When normalized plots of $\epsilon'' - T$ show that the high temperature peaks merge into a single curve suggesting that the peak height is independent of water content. The lower temperature peaks do not merge into a single

curve. The peaks are attributed to water residing in two different sites. One is the oxygen of the ether linkage and the other is one of the four carbonyl groups. At low humidity the latter is more likely to be the host. Since the activation energy for the high energy peak is determined as 0.53 eV, which is twice that of a hydrogen bond, both bonds of a water molecule are likely to be involved in the relaxation process.

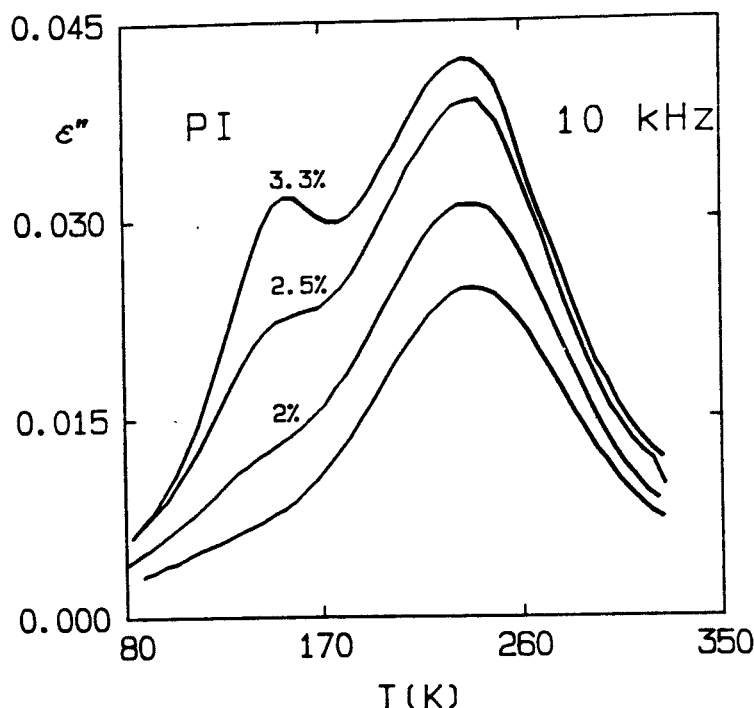


Fig. 5.37 ϵ'' of PI films containing different amounts of water at 10 kHz. For the lowest curve the film was dried for two days in vacuum, for the other curves the water content is given in wt% (Melcher et. al. 1989, with permission of Trans. Diel. Elec. Insul.)

5.5 SCALING METHODS

We have seen that a large number of liquids could be cooled very slowly, that is super cooled, into an amorphous solid called glass. As the liquid cools its relaxation time increases and at the glass transition temperature the relaxation time τ increases even more rapidly. The Arrhenius law does not hold any more and the relaxation time at the transition region is given by the Vogel-Fulcher law, equation (5.20). We have also seen that many polymers show agreement with different expressions over a limited range of temperatures, but no general expression appears to have been successful in covering the entire range of temperature in the super cooled state. Since τ is a strong function of T and hence a strong function of $1 / \omega$, a large range of frequency needs to be considered before deciding whether any particular scheme is general and applicable to a large number of materials.

Moreover the shape of the complex plane plot changes from a near Debye semi-circular shape to that described by Cole-Cole arc, Davidson-Cole's skewed arc and Havriliak and Negami function. The latter has been particularly successful in the vicinity of the transition temperature. In an attempt to find a general expression, several scaling methods have been suggested and we describe the method adopted by Nixon et. al.⁸⁶ as it extends over a wider range of frequency from $10^{-3} \text{ Hz} \leq f \leq 10^{+10} \text{ Hz}$. Many samples were measured including glycerol which we have discussed in connection with Davidson-Cole expression. A difficulty usually encountered in designing a suitable scaling law is that the primary relaxation overlaps a secondary relaxation, and in such cases the frequency range needs to be chosen appropriately to make sure that only primary relaxation is covered.

Both ϵ' and ϵ'' were measured by Nixon et. al. (1990) combining a number of different techniques to cover a wide range of frequency. At low frequencies below 10^{-4} time domain measurements were carried out. In the range $10 \text{ k Hz} < f < 10 \text{ MHz}$ four probe impedance measurements were adopted. For frequencies greater than 50 MHz, data were taken in both transmission and reflection with a 50Ω co-axial transmission line and network analyzer.

The factors involved in the scaling law of Nixon et. al. are the loss factor ϵ'' , f , f_{max} , the dielectric decrement $\Delta\epsilon$, and the width of the loss factor curve at half peak W . For Debye relaxation which has a single relaxation time this width, W_D is $\cong 1.14$ decades. The width is normalized according to $w \equiv W/W_D$. This is acceptable because the narrowest width for any material is the Debye width. We recall that as the temperature increases, f_{max} also increases and the width of the loss factor curves becomes smaller.

The familiar $\log_{10}(f_{max}\text{-Hz})$ versus $1/T$ curves show similar behavior though displaced from each other. However the increase occurs in different ways resulting in a curve for each material. The purpose of scaling is to find a scheme in which all of the data fall on a single curve.

The scaling law proposed consists of plotting

$$x = \frac{1}{w} \left(1 + \frac{1}{w}\right) \log_{10} \left(\frac{f}{f_{max}}\right); y = \frac{1}{w} \log_{10} \left(\frac{\epsilon'' f_{max}}{\Delta\epsilon f}\right) \quad (5.23)$$

The factor f_{max}/f for the y-axis aligns the peaks of the loss factor curves and the entire term normalizes the curves to the same half width. Fig. (5.38) shows that data for all seven materials investigated by Nixon, et al. fall on a single curve verifying the applicability of the proposed scheme. Though the scaling methods provide a compact

way of providing data for a large number of polymers its use in interpreting the measured values in terms of morphology is limited.

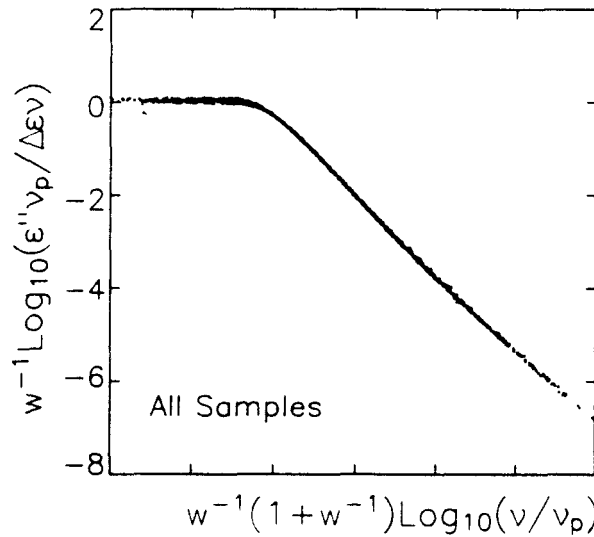


Fig. 5.38 Scaling law for several polymers proposed by Nixon et. al. (1990). (with permission of AIP)

5.6 CONCLUDING REMARKS

An attempt, however concise, has been made in the previous pages to describe the relaxation processes that occur in polymers. The present summary includes only the polymers which we have discussed except where a reference is required for other polymers. The classification of relaxation peaks is mainly according to Hoffmann, et al. (1966). The relation between temperature and frequency for the same peak is such that lowest frequency correspond to the highest temperature. In crystalline polymers α_c -relaxation occurs at the lowest frequency and the highest temperature, $T/T_m \sim 0.9-1.0$. With decreasing temperature and increasing frequency γ_c and δ_c relaxations occur in that order. The β -relaxation is not observed in single crystals.

Semi-crystalline polymers exhibit α_c -, β_a -, γ_c -, γ_a -, and δ_c -relaxations. α_c -mechanism occurs close to T_m and β -mechanism just above T_G . The γ -peak occurs just below T_G . One of the methods used to ascertain the region in which relaxation occurs is to use samples of varying crystallinity, if that is possible at all, and relate the magnitude of the loss peak with the degree of crystallinity. In highly crystalline polymers having crystallinity of $\sim 90\%$, such as high density polyethylene, it is difficult to visualize a distinct amorphous phase; it may be more appropriate to think in terms of motion in disordered region and in-between crystallites⁸⁷.

In wholly amorphous polymers α -relaxation is absent, β -relaxation occurs at $\sim T_G$ and γ -relaxation at lower temperatures. This designation, though not practiced uniformly, makes the nomenclature for crystalline and amorphous polymers uniform (Bur, 1984).

For each relaxation process, increase of temperature increases the frequency at which the loss peak is observed. Plotting f_{max} versus $1/T$ yields a relaxation map and from these plots the activation energy for each process is obtained. The energy increases generally in the order of δ -peak to α -peak. For most polymers the activation energy $\epsilon_\beta / \epsilon_\alpha \ll 1$. This means that the β -peak is less pronounced than the α -peak. This is true in the case of isotactic PMMA (Fig. 5.40) but the syndiotactic PMMA exhibits a contrary behavior. The inset of fig. 5.26 may be referred to, to see this. In fact the ratio of $\epsilon_\beta / \epsilon_\alpha$ has been shown to gradually increase and exceed a value of one as the tacticity of PMMA is systematically increased from isotactic to syndiotactic polymer.

Recent advances in the study of PMMA are measurements carried out on free standing very thin films of polymers, in the range of ~ 10 nm⁸⁸. Thin polymer layers exhibit a glass transition temperature that is dependent on the thickness and the explanations for this observed phenomenon are not yet clear. Further, nanometer thick polymers play an important role in coatings and knowledge of molecular dynamics is highly desired.

Fig. 5.39 shows the dielectric loss ϵ'' versus frequency for isotactic PMMA having a sample thickness of 21 nm (molecular weight 44900 g mol⁻¹) at various temperatures. The bulk properties are reproduced well in thin films. At lower temperatures, in the range 305 K-325 K, only the β -relaxation is present. From the top figure, it is noted that at 325 K, the high frequency wing of the α -relaxation appears. The higher temperature dielectric loss in the region of 329 - 357 K shows the region of merging of α - and β -relaxations. The inset shows the separation of the two relaxations.

Fig. 5.40 shows that the β -relaxation has a lower activation energy when compared with the α -relaxation. Further the β -relaxation follows the Arrhenius law and the α -relaxation follows the Volger-Fulcher-Tamann law. The inset shows the shift of the α -relaxation to lower temperatures as the thickness increases with the bulk having the lowest T_g . T_g is determined by the intersection of the relaxation curve with the line $1/\tau_{max} = 10^{-2}$ Hz, as shown by the dashed line in fig. 5.40.

The dielectric properties of polyimide has received considerable attention in recent years, due to the possibility of modifying its dielectric properties by various means. A low dielectric constant is preferred for several applications, such as an inter layer medium in multilayer integrated circuits. Addition of fluorine appears to lower the dielectric constant to a value close to 1.9 when compared with the value of ~ 2.6 -3.1

without this addition. There is experimental evidence to show that irradiation by high energy beams also reduces the dielectric constant.

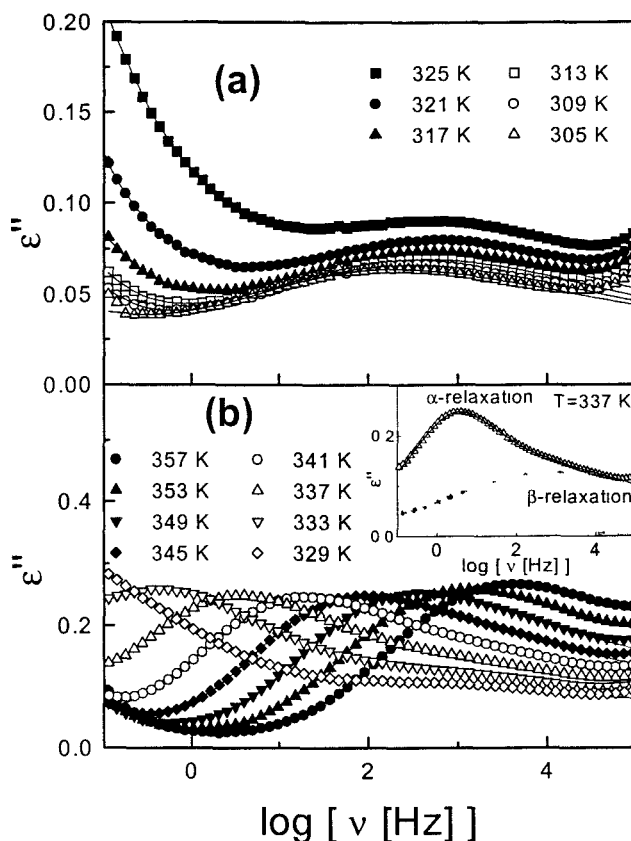


Fig. 5.39 Dielectric loss factor in thin film of isotactic PMMA. The top figure shows the relaxation in at lower temperatures. The bottom figure shows the merger of both α - and β -relaxation at higher temperatures. The inset in the bottom figure shows the separated relaxations at 337 K. Note the difference in the scale for dielectric loss in (a) and (b). (Kremer and Hartmann, 2001: Dielectric News Letter)

Recent results of Alegaonkar et. al.⁸⁹ provide quantitative results for polyimide which is irradiated by an electron beam of 1 MeV energy. The measured loss factor is shown in fig. 5.41 for various flux of the electron beam at room temperature and two peaks are seen, one at a frequency of $\sim 10^4 \text{ Hz}$ and the other, a much larger one at $\sim 1 \text{ MHz}$. The higher frequency relaxation is broader suggesting a distribution of relaxation times. The higher loss with increasing flux is ascribed to conversion of crystalline regions to amorphous ones, increasing the disorder in the material. Further support to this reasoning is obtained by the observation that the density of the polyimide is lowered with increasing flux. This effect also explains the lowering of the dielectric constant (fig. 5.42). The lowering of the dielectric constant with cobalt-60 irradiation occurs due to the fact that the gamma rays generate defects in the polyimide into which Boron or fluorine atoms diffuse and the polarization is lowered.

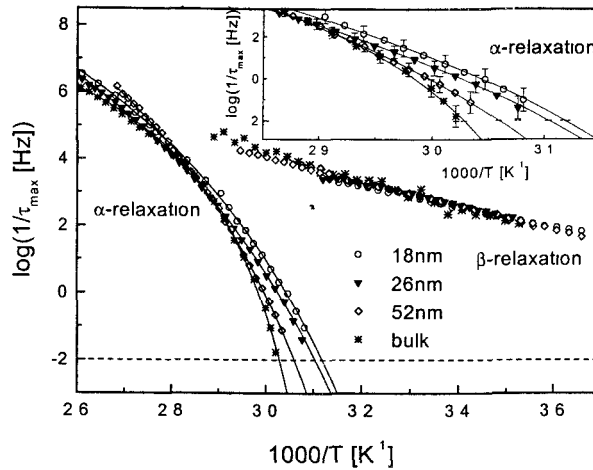


Fig. 5.40 Logarithm of the reciprocal of relaxation time corresponding to the maximum frequency as a function of $1/T$ in isotactic PMMA. The thickness of the film is the parameter (Kremer and Hartmann, 2001: Dielectric News Letter).

Polymeric insulation is extensively used in power equipments such as motors, transformers, cables and capacitors. The insulation is subjected to high electrical stress of the order of 20 MV/m, though this films have a much higher dielectric strength. The degradation that occurs in the material is a major cause of worry to design and operating engineers. The phenomenon of electro-luminescence, that is the generation of light due to electrical stress is the precursor of progressive deterioration and inception of partial discharges. Bamji and colleagues^{90, 91} have studied this phenomenon in polyethylene.

Semi-crystalline polymers exhibit both α -and β -relaxations both of which are well defined. At temperatures $T \sim T_G$ the α -relaxation is due to the micro-Brownian motion of main chains and at $T < T_G$ the β -relaxation occurs. The ϵ'' - $\log \omega$ plots for β -relaxation curves are quite broad when compared with those for the α -relaxation.

The β -relaxation is usually attributed to the motion of side groups. In linear chain polymers with no branches segmental motion occurs. The segmental motion is frozen far below glass transition temperature, but considerable local motion such as rotation or rotational oscillation may exist at lower temperatures. Each mode is associated with a characteristic temperature and frequency.

In highly crystalline polymers, as in high density polyethylene, the α -relaxation is due to reorientation of the chain within the lamella or extended chain crystal. For short chains the reorientation occurs as a rigid rod but as chain length increases rotation-translation assisted by twisting of the chain is the process for the primary relaxation. The β -relaxation in polyethylene is due to large scale micro-Brownian motion in the disordered regions between the crystallites.

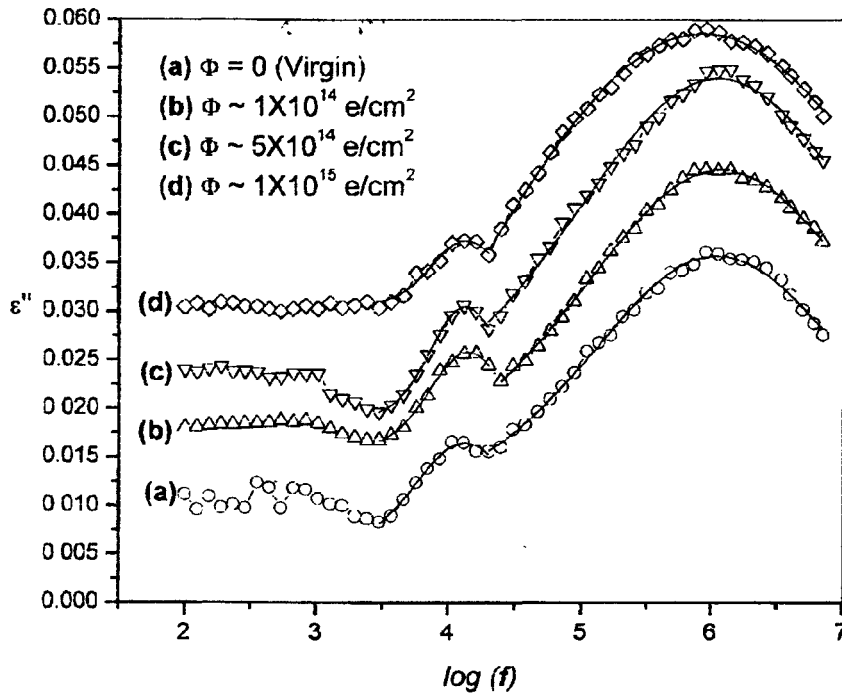


Fig. 5.41 Variation in the loss factor with frequency for polyimide samples irradiated with 1 MeV electrons at various electron flux (Algaonkar et. al. 2002, permission of A I P).

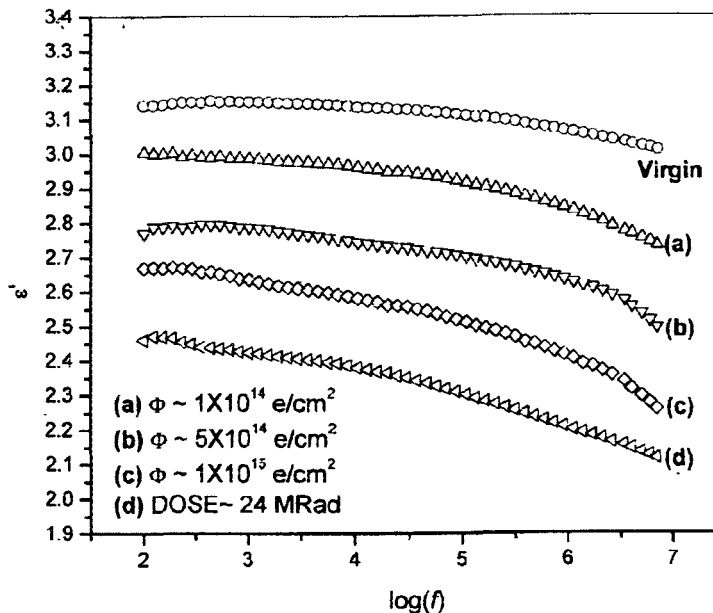


Fig. 5.42 Variation in dielectric constant with frequency for polyimide samples irradiated with 1 MeV electrons at different flux, ϕ . Plots a, b, c are for electron irradiated samples, plot d for sample irradiated with gamma ray and immersed in BF_3 solution. (Algaonkar et. al. 2002, permission of Amer. Inst. Phys.)

The origin of the γ -relaxation in polyethylene is not quite clear and attributed to impurities. The number of dipoles exhibiting this type of relaxation increases with decreasing crystallinity suggesting that the process occurs in the amorphous regions. In PCTFE the γ -relaxation has two components, designated as γ_c and γ_a one in the wholly crystalline region and the other in the wholly amorphous region. In polyethylene and PCTFE the γ -relaxation makes the dielectric loss curves very broad at low temperatures and the curves become narrower as the temperature is increased.

The studies on a large number of polymers have provided insight into the molecular motion in amorphous and crystalline solids. The methods of correlating the results of dielectric studies with the structure of solids continue to be a fruitful area of research. A quick-glance pictorial of relaxation in some of the polymers discussed is provided in Fig. 5.43.

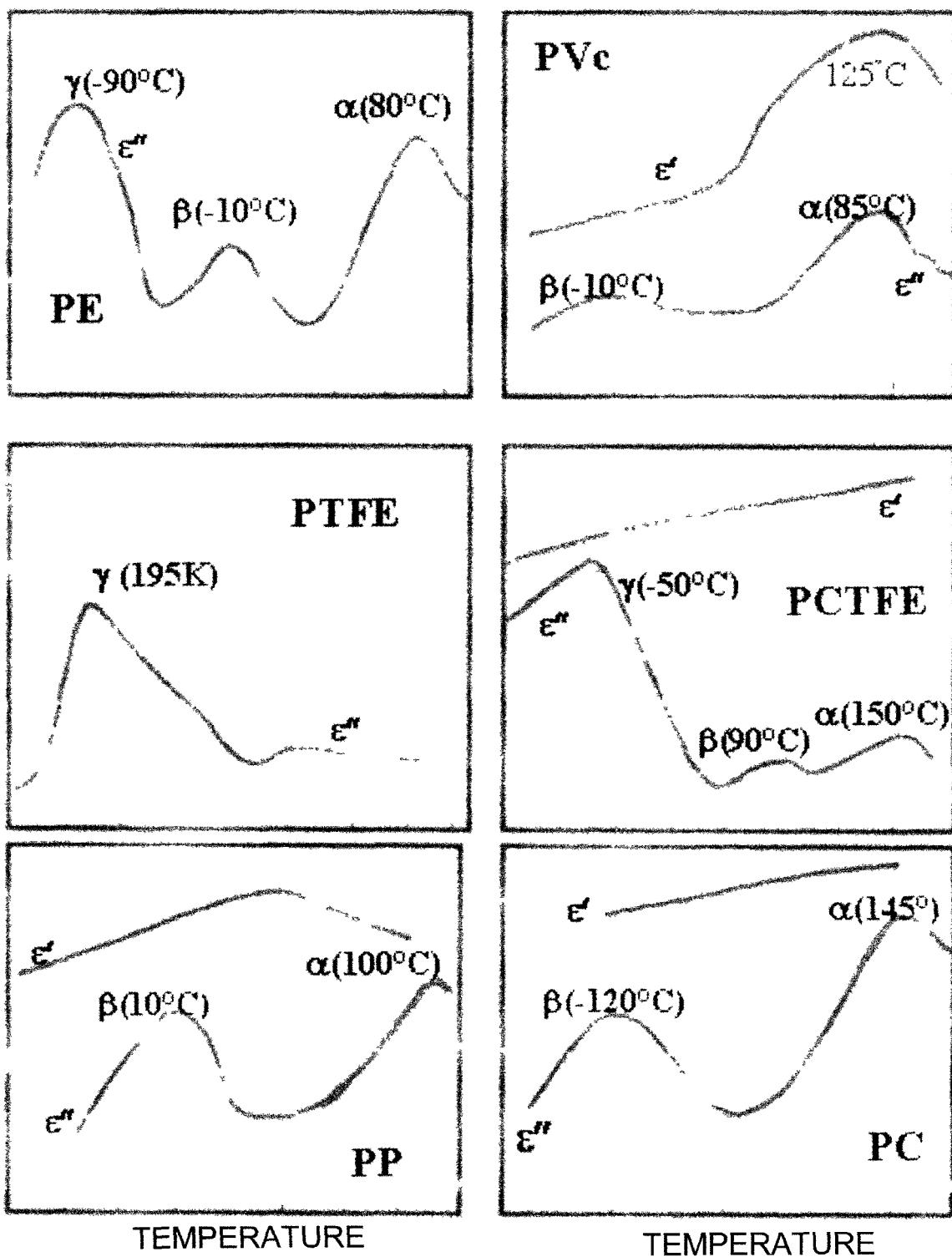


Fig. 5.43 Quick reference for relaxation mechanisms in selected polymers.

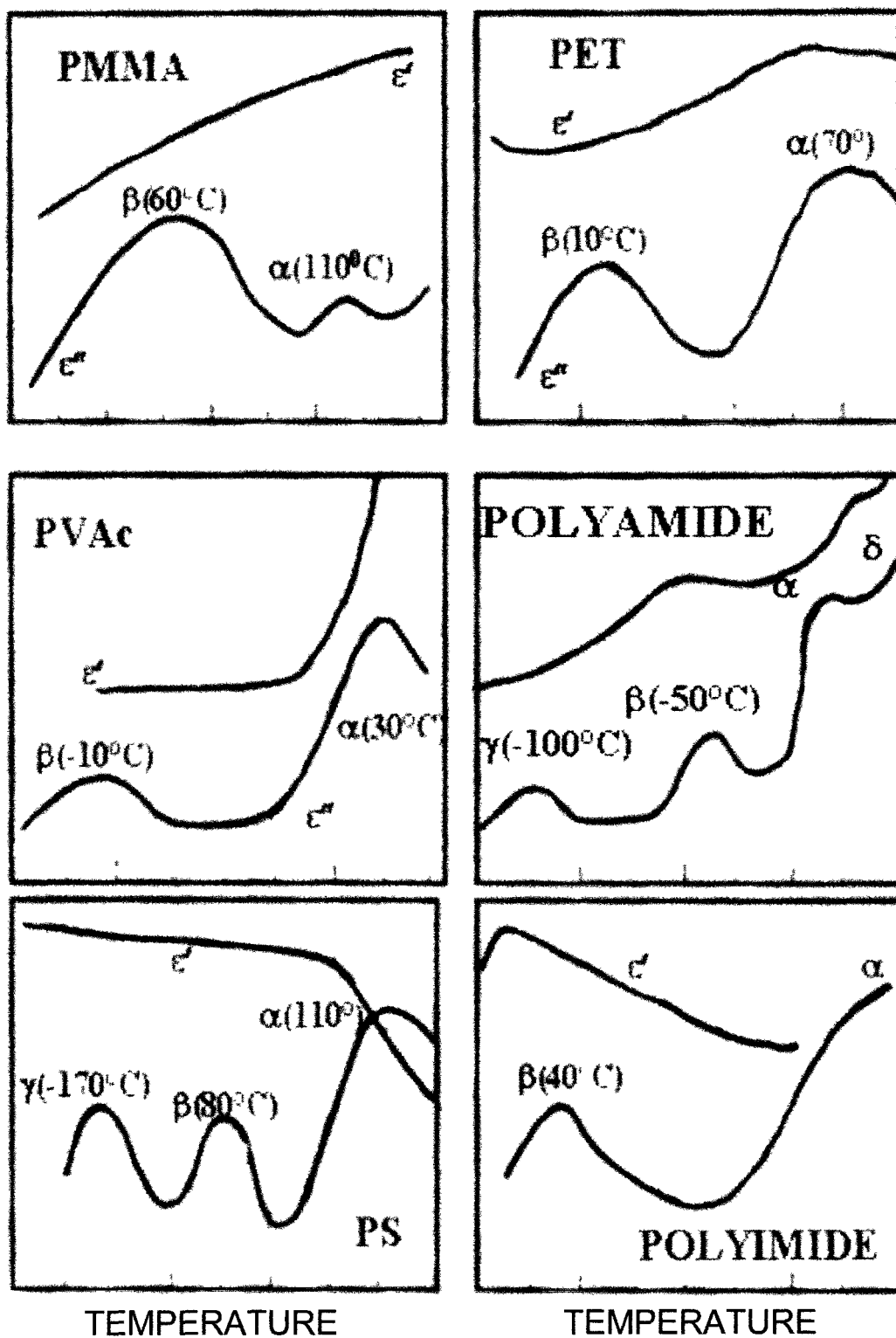


Fig. 5.43 (contd.). Quick reference of relaxation mechanisms in selected polymers.

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